

STUDIES ON MIXED COMPLEXES

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by
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to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
JULY, 1977

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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India under the supervision of Professor A. Chakravorty.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made whenever the work described is based on the findings of other investigators.

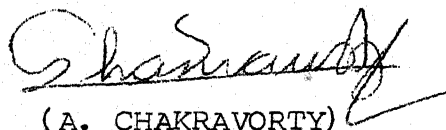
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Certified that the work 'STUDIES ON MIXED COMPLEXES' has been carried out under my supervision and the same has not been submitted elsewhere for a degree.



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Thesis Supervisor

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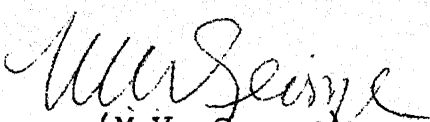
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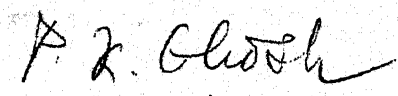
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Mr. B.S. Raghavendra was admitted to the candidacy of the Ph.D. degree programme in April 1975 after he successfully completed the written and oral qualifying examinations.


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B.S. Raghavendra

PREFACE

Much of the chemistry described in this thesis can be broadly divided under two headings: (i) mixed-ligand type and (ii) mixed-metal type. Our original interest in mixed complexes centred around mixed ligand complexes of composition $M(Lb)(Lt)$, where Lb and Lt are potentially bidentate and tridentate ligands. Old results are summarised in Chapter I and new results are presented in Chapters II and III. Examples of the type $M(\text{ligand})_n X_n$, where X is a halogen atom can be found in Chapter IV. In Chapters IV and V the ligand systems used contain the azoimine fragment. The mixed metal complexes of Chapter V include the combination Fe(II), Na(I); Fe(II), Fe(III). The latter comes under the mixed valence category. Many new molecular systems are described in this thesis. The major emphasis is on structure elucidation using a number of spectroscopic, magnetic and other techniques. Admittedly the final answer to a structural problem lies in most cases in diffraction work. Yet there is joy in trying to grope in dimmer light of indirect techniques, the shape of these molecules. We have enjoyed doing the little that has been reported in the pages to follow. Our efforts will remain fully rewarded if the reader finds at least a few enjoyable items. In spite of all attempts, unintentional oversights and errors will be present in the thesis. The author is responsible for all this.

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CHAPTER I

SOME ASPECTS OF THE M(bidentate)(tridentate) SYSTEM

Abstract: The stereochemical pattern in various mixed-ligand systems of the type M(bidentate)(tridentate) are reviewed in this chapter. Examples are cited where the metal atom is penta-coordinated. In other cases octahedral geometry results from dimerisation or adduct formation. In a number of cases stereochemical equilibria are identifiable in the solution phase.

I.1 INTRODUCTION

The work described in the next two chapters originated as part of our studies on the design of mixed-ligand molecules of the type $M(\text{bidentate})(\text{tridentate})$. Some synthetic and structural aspects pertaining to this system are summarised in this chapter.

I.2 GENERAL CONSIDERATION

A monomeric complex of the formula $M(\text{Lb})(\text{Lt})$ (where Lb = bidentate ligand and Lt = tridentate ligand) in which all the potential coordinating atoms are bonded to metal will be pentacoordinated. This is a very simple strategy which however, has been rarely used in practice. Examples will be given in the next section.

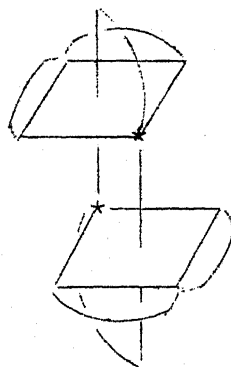
The occurrence of pentacoordination in $M(\text{Lb})(\text{Lt})$ systems may be hindered by various factors some of which are noted below:

(i) Facile disproportionation reaction



in which the products need not have pentacoordinated geometry.

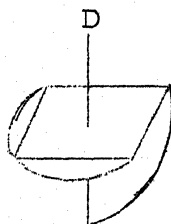
(ii) Dimerisation Leading to $M_2(Lb)_2(Lt)_2$ in which the metal atom may be pseudooctahedral as shown below (I):



* = bridging atom

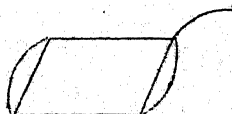
(I)

(iii) Adduct formation with Lewis base (D) giving pseudooctahedral geometry (II):



(II)

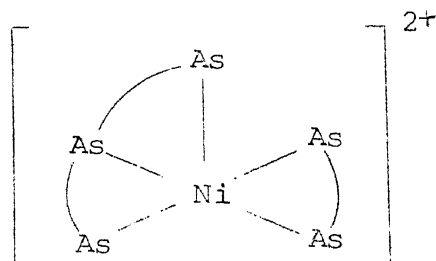
(iv) Lack of complete coordination for example, the Lt unit can actually act as a bidentate ligand giving rise to four-coordinated complexes (III):



(III)

I.3 SOME RESULTS

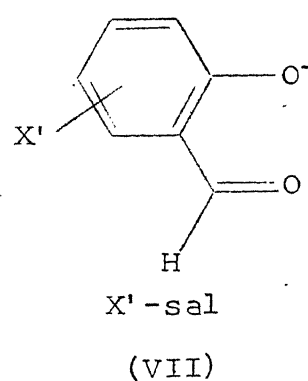
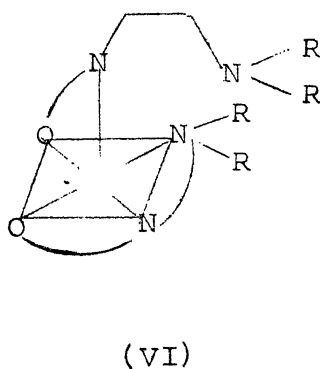
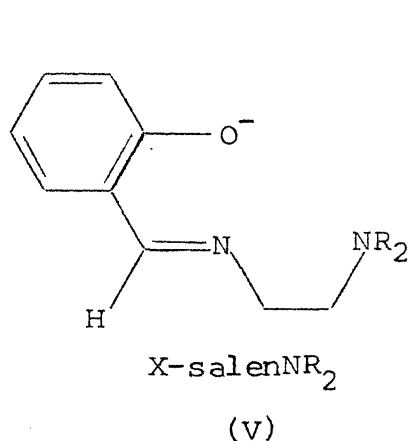
The best known early example belonging to the $M(Lb)(Lt)$ class is probably $M(diars)(triars)^{2+}$ which is low-spin and has the sp coordination sphere as shown in (IV):



(IV)

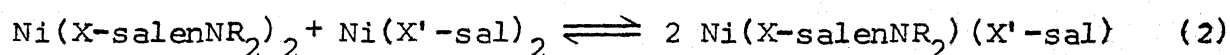
The synthesis and identification of this complex has an interesting history.¹⁻³ It was first obtained under conditions when no one expected it. Eventually however, it was prepared by reacting nickel(II) perchlorate with a mixture of diars and triars. Recently a similar complex having the $NiAs_4Sb$ coordination sphere is reported.⁴

Certain bis complexes of the Schiff bases of the type (V) have been shown to have pentacoordinated geometry:



Examples are: $M(5\text{-Cl-salenNET}_2)_2$ ^{5,6} ($M = \text{Ni(II)}, \text{Co(II)}$) and $\text{Cu(salenNMe}_2)_2$ ⁷. In these cases the ligands are potentially tridentate. However, in the bis complexes one of the two ligands uses only two of the three coordinating positions (probably due to steric reasons) as shown in (VI). These complexes, therefore, do not strictly belong to the class $M(\text{Lb})(\text{Lt})$ as defined above.

Reactions of the type:



have been identified to occur in solution.⁸ The complexes on the right hand side are pentacoordinated and do belong to the class $M(\text{Lb})(\text{Lt})$, X'-sal being bidentate (VII). Equilibria belonging to the type (2) has also been observed in the case of triazine-1-oxide system.⁹

A few years ago we were attracted by the simplicity of the little used $M(\text{Lb})(\text{Lt})$ strategy. We undertook a project on the synthesis, structural characterization, and reactions of new $M(\text{Lb})(\text{Lt})$ species in which Lb has only oxygen donors (acetylacetone, salicylaldehyde anions or their derivatives) and Lt belongs to the type (V). The results will be summarised below. Before this is done the abbreviations used for the ligand systems are stated.

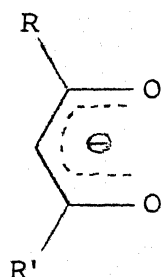
X' -sal \equiv structure VII, when $X' = H$, X' -sal will be written as sal,

X -salenNR₂ \equiv structure V, when $X = H$, X -salenNR₂ will be written as salenNR₂,

bdk = conjugate base of β -diketone (structure VIII),

ac = conjugate base of acetylacetone (structure VIII, $R = R' = CH_3$),

bz = conjugate base of benzoylacetone (structure VIII, $R = CH_3$ and $R' = C_6H_5$).

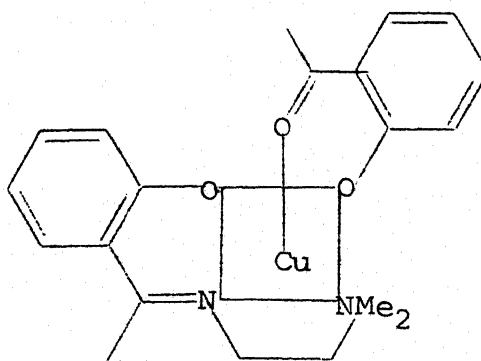


(VIII)

System $Cu(X'$ -sal)(X -salNR₂)

In our attempts to generate these systems, we were particularly encouraged by the report of Pfeiffer and Krebs¹⁰ that $Cu(sal)_2$ reacts with N,N -diethylethylenediamine to give rise to a green complex of empirical formula $Cu(sal)(salenNEt_2)$. We have shown^{11,12} that the reaction of $Cu(X'$ -sal)₂ and N,N -diethylethylenediamine taken in the molar ratio 1:1 in toluene provides an efficient, neat and general method for the synthesis of $Cu(X'$ -sal)(X -salenNR₂). These (i) are monomolecular in solution, (ii) give rise to C=N, C=O stretches in the infrared, (iii) show two electronic bands in the region 710-580 nm,

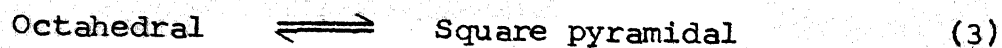
(iv) exhibit an axial epr spectrum with $g_{\perp} \sim 2.06$ and $g_{\parallel} \sim 2.24$. On the basis of these and other evidences it was concluded that $\text{Cu}(\text{X}'\text{-sal})(\text{X-salenNR}_2)$ are pentacoordinated, probably with square pyramidal geometry. This has been fully corroborated by three dimensional X-ray structural work¹³ on $\text{Cu}(\text{sal})(\text{salenNMe}_2)$ (IX). The reactivity of $\text{Cu}(\text{X}'\text{-sal})(\text{X-salenNR}_2)$ towards acids and other reagents has been examined.^{11,12}



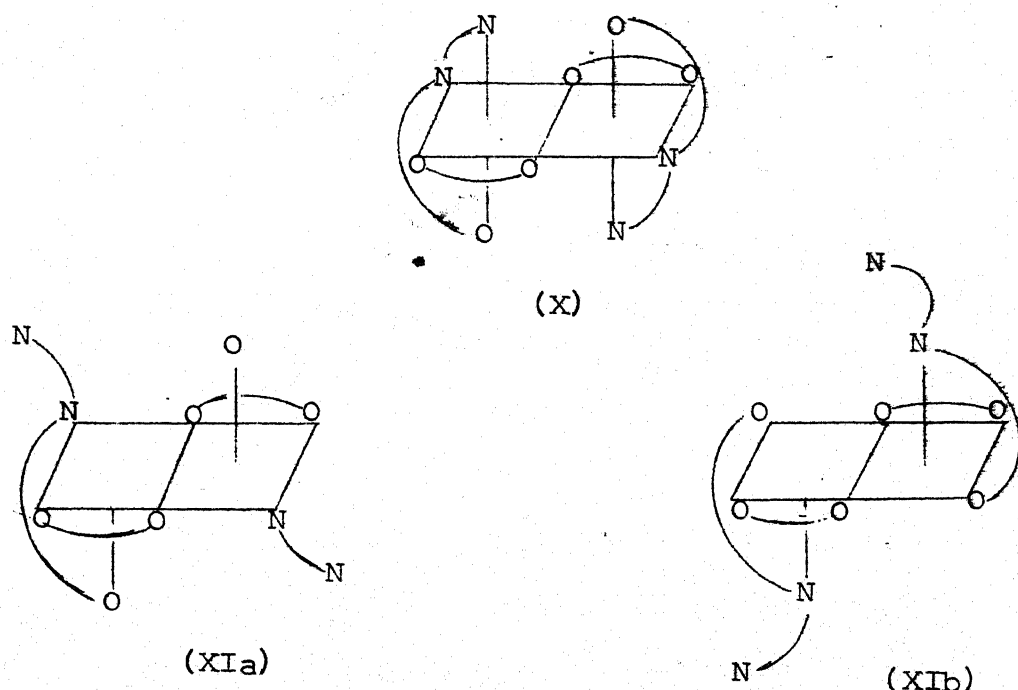
(IX)

System $\text{Ni}_2(\text{sal})_2(\text{salenNR}_2)_2$ ^{14,15}

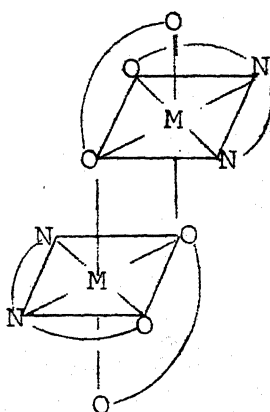
These dimeric species are fully paramagnetic (~ 3.10 B.M. per nickel) in the solid state and in solution over a wide range of temperature. The electronic spectrum in the solid state is characteristic of an octahedral geometry for nickel(II) ($\nu_1 \sim 935$ nm and $\nu_2 \sim 610$ nm). Spectra in solution (benzene, chloroform) are temperature dependent due to the existence of the equilibrium



The pentacoordinated species shows a ligand field band at ~ 1335 nm, whose intensity increases with increasing temperature, showing that equilibrium (3) shifts to the right as temperature is raised. It has been proposed that the octahedral species has the structure X, while the square pyramidal could be either XIa or XIb. All the species are high-spin. It was seen earlier that $\text{Cu}(\text{sal})(\text{salenNR}_2)$ is monomeric and square-



pyramidal. The nickel(II) dimer arises by simple stacking of two copper(II)-like monomers (IX) one above the other in a manner shown in XII, which is of course equivalent to (X). The nickel(II) species provide an example where pentacoordination in $\text{M}(\text{Ib})(\text{Lt})$ is hindered by dimerisation (see Section I.2). It is known that unlike copper(II), nickel(II) has a higher affinity

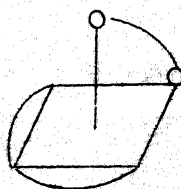


(XII)

for hexacoordinated geometry as compared to pentacoordinated geometry. The $M(X'-sal)(X-salenNR_2)$ system provides an additional example.

System $Cu(ac)(salenNR_2)^{16}$

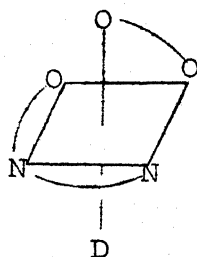
These are formed when $[Cu(ac)(OCH_3)]_2$ and tridentate Schiff base are refluxed in 1:2 ratio in methanol. On the basis of spectral and magnetic studies $Cu(ac)(salenNMe_2)$ has been suggested to have a square pyramidal geometry both in the solid and in solution (XIII, compare with IX). On the other hand, $Cu(ac)(salenNEt_2)$ forms a pseudooctahedral methanol adduct in the solid state which loses methanol on dissolution with benzene.



(XIII)

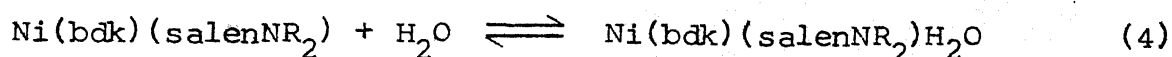
System Ni(bdk)(salenNR₂)¹⁷⁻¹⁹

When bis(bdk)nickel(II) (hydrated or anhydrous) (1 mol) is reacted with the Schiff base salenNR₂ (1 mol) in boiling toluene and the resulting brown solution is left to crystallise in open air (which supplies moisture), shining green crystals of composition Ni(bdk)(salenNR₂)(OH₂) deposit (where bdk = ac or bz). Alternatively Ni(ac)(salenNR₂)(OH₂) can be obtained by reacting Ni(ac)₂·2H₂O with Ni(salenNR₂)₂ or Ni(salenNR₂)₂ with Hac in equimolecular amounts in boiling toluene followed by open air crystallisation. When heated in the range 80-100°C at 5 mm the green crystals slowly disintegrate to a brown mass which when cooled becomes a glassy solid. During this process water is lost, the maximum loss corresponding to one mole of water per mole of the complex. The composition of glassy mass is found to be Ni(ac)(salenNR₂). When this is crystallised from moist solvents the crystals of Ni(ac)(salenNR₂)(OH₂) is regenerated. From solvents containing pyridine (py) crystals of Ni(ac)-(salenNR₂)(py) can be readily obtained. This system is monomolecular in benzene solution. In the solid state Ni(ac)(salenNR₂)(D) (D = H₂O, pyridine) is fully paramagnetic. It is octahedral (XIV) in the solid state. On the other hand, the anhydrous species show electronic spectra characteristic of high-spin square pyramidal nickel(II) (${}^3B_1(F) \rightarrow {}^3E(F) \sim 1370 \text{ nm}$; ${}^3B_1(F) \rightarrow {}^3A_2(F) \sim 950 \text{ nm}$; ${}^3B_1(F) \rightarrow {}^3B_2(F) \sim 770 \text{ nm}$; ${}^3B_1(F) \rightarrow {}^3E(F) \sim 600 \text{ nm}$).



(XIV)

They belong to the structural type (XIII). In solution (benzene, chloroform) the equilibrium



is observed. On the basis of variable temperature spectral data, the thermodynamic parameters for this equilibrium have been determined to be $\Delta H^\circ = -13(\pm 1) \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -38(\pm 5) \text{ eu}$. For a given compound, the population of pentacoordinate species for a given solvent has the order benzene < chloroform < nitrobenzene. In these systems, pentacoordination is hindered by adduct formation (see Section I.2).

System $\text{Co}(\text{ac})(\text{salenNR}_2)^{20}$

These are readily obtained by reacting bis(acetylacetonato)-cobalt(II) with the Schiff base in boiling toluene. On the basis of magnetic and spectral data it has been concluded that

$\text{Co}(\text{ac})(\text{salenNET}_2)$ belongs to the structural type XIII (square-pyramidal) both in solid state and in solution. On the other hand $\text{Co}(\text{ac})(\text{salenNMe}_2)$ is octahedral (dimerisation, structural type X) in the solid state. But it becomes pentacoordinated in solution.

All results stated above are summarised in Table I.1.

TABLE I.1

STEREOCHEMISTRY OF M(Lb)(Lt) SYSTEMS

System	Molecu- larity	Structure		Comments
		Solid	Solution	
Cu(sal)(salenNR ₂)	Monomer	SP	SP	Ideal M(Lb)(Lt) system.
Ni(sal)(salenNR ₂)	Dimer	O	SP \rightleftharpoons O	Pentacoordina- tion partially hin- dered by dimeri- sation.
Cu(ac)(salenNR ₂)	Monomer	SP ^a	SP	-
Ni(bdk)(salenNR ₂)H ₂ O	"	O	SP + H ₂ O \rightleftharpoons O	Adduct forma- tion hinders pentacoordina- tion.
Ni(bdk)(salenNR ₂)	"	SP	SP	-
Co(ac)(salenNR ₂) ^b	-	SP or O	SP	Pentacoordina- tion partially hindered by di- merisation.

a, Cu(ac)(salenNEt₂)CH₃OH is pseudooctahedral in solid state.

b, Not soluble enough for molecular weight measurement.

SP, Square pyramidal.

O, Octahedral.

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CHAPTER II

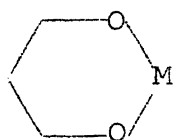
SOME PYRROLE BASED MIXED COMPLEXES^{*}

Abstract: New systems of the type $M(\text{pyrenNR}_2)\text{Br}$, $M(\text{pyrtnNR}_2)\text{Br}$ ($M = \text{Cu}, \text{Ni}$), $M(\text{pyr})(\text{pyrenNR}_2)$ ($M = \text{Cu}, \text{Ni}$), $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ (where Hpyr is pyrrole-2-aldehyde, pyrenNR_2 is Schiff base of pyr and $\text{NR}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and pyrtnNR_2 is Schiff base of pyr and $\text{NR}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) are reported. The first two systems are shown to have planar geometry in which pyrenNR_2 and pyrtnNR_2 act as tridentate ligands. On the basis of magnetic, spectral and X-ray powder diffraction studies on pure crystals and on solid solutions of nickel(II) and copper(II) species, it is concluded that $M(\text{pyr})(\text{pyrenNR}_2)$ has a tetracoordinate grossly planar geometry in which the NR_2 group of pyrenNR_2 fails to occupy a coordination position due to steric overcrowding. The powder epr spectrum of $\text{Ni}(\text{pyr})(\text{pyrenNR}_2)$ doped with the corresponding copper(II) species is axial showing both hyperfine (in parallel region) and superhyperfine (in perpendicular region) splittings. Models demonstrate that this steric difficulty mentioned above should considerably decrease on replacement of pyrenNR_2 by pyrtnNR_2 . Indeed the species $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ have electronic spectra strongly suggestive of pentacoordination.

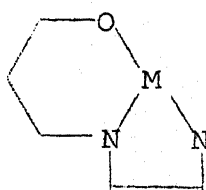
^{*}The work described in this chapter has appeared in *Inorg. Chim. Acta*, 18, 257 (1976).

II.1 INTRODUCTION

In most systems described in the last chapter the M(bidentate)(tridentate) unit shows the coordination pattern I for the bidentate and II for the tridentate ligand. In total

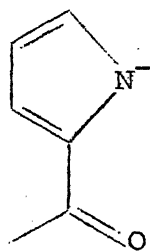


(I)

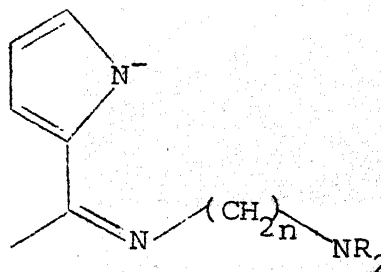


(II)

three oxygen and two nitrogen atoms are involved in coordination and two out of the three chelate rings are six-membered. We wanted to investigate the structural effect of making more chelate rings five membered and more coordinating atoms nitrogen. We therefore investigated the synthesis and structure of systems based on pyrrole-2-aldehyde (Hpyr) and its Schiff base with $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NR}_2$ ($n = 2$ or 3). The conjugate base of these species are shown in III and IV. III will be abbreviated as pyr, while



(III)

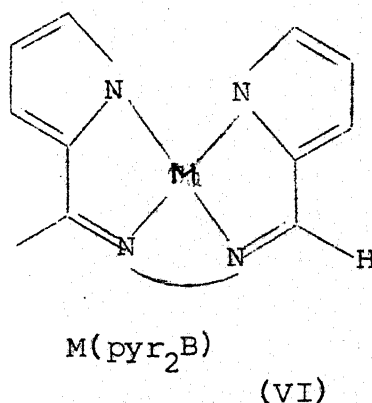
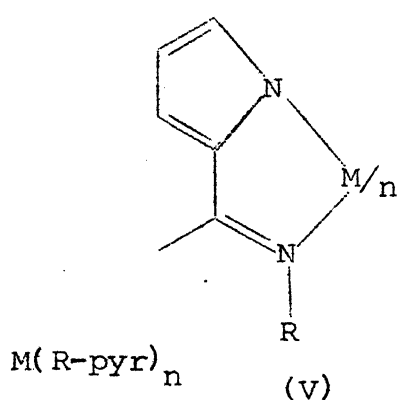


(IV)

the abbreviation for IV will be pyren NR_2 (when $n = 2$) and

pyrtnNR₂ (when n = 3). The corresponding neutral Schiff bases will be called HpyrenNR₂ and HpyrtnNR₂.

The pyrrole-2-alimine group (refer to IV) is a fragment of biomolecules such as porphyrins. In this regard the pyrrole-2-alimine complexes are of peripheral biochemical interest. There are a few reports^{1,2} on the chelates of pyrrole-2-alimines. All of these deal with the structural type M(R-pyr)_n (V) and M(pyr₂B) (VI). The potentially tridentate ligand obtained by condensing Hpyr and ethanolamine gives Cu(pyr-ethanolamine) when refluxed with copper acetate in methanol.³ The bis chelate of pyrrole-2-aldehyde, Cu(pyr)₂ is also described.⁴ No mixed ligand species based on ligands III and IV are reported in literature (except our own work).

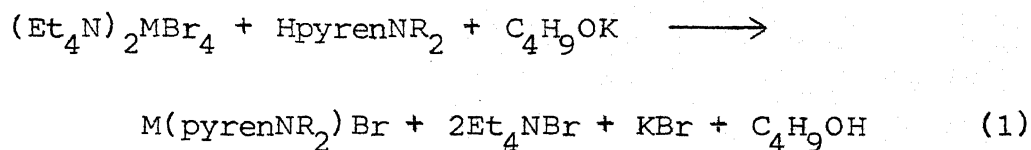


II.2 RESULTS AND DISCUSSION

A. Syntheses

The following systems have been obtained in the present work: M(pyrenNR₂)Br, M(pyrtnNR₂)Br, M(pyr)(pyrenNR₂), Cu(pyr)-(pyrtnNR₂) (M = Cu or Ni).

M(pyrenNR₂)Br and M(pyrtnNR₂)Br were obtained as dark coloured shining crystals by reacting (Et₄N)₂MBr₄ with the Schiff base in presence of strong base such as potassium-t-butoxide in tetrahydrofuran (non-aqueous chelation reaction). The overall synthetic reaction is

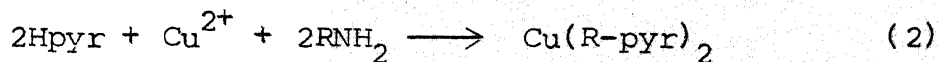


A similar reaction can be written for the pyrtnNR₂ system.

Brown crystals of Ni(pyr)(pyrenNMe₂) were obtained by a similar nonaqueous chelation reaction involving (Et₄N)₂NiBr₄, Hpyr, HpyrenNMe₂ and base.

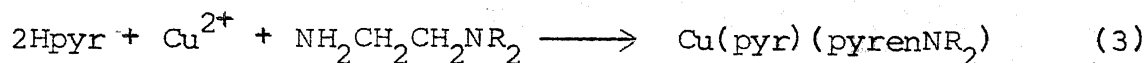
Green crystals of Cu(pyr)(pyrenNR₂) and Cu(pyr)(pyrtnNR₂) were obtained by aqueous reactions.

Pyrrole-2-alimine complexes of copper(II) of type (V) are readily obtained² by the following reaction in aqueous media:

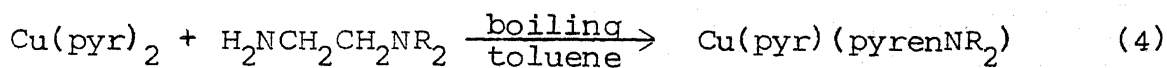


However, when RNH₂ is replaced by N,N-disubstituted ethylene-diamine green crystals of mixed ligand complex of composition Cu(pyr)(pyrenNR₂) are readily deposited. The second pyr moiety

does not undergo Schiff base condensation even when excess amine is used. The observed reaction can be written as:



The mixed ligand complexes are also obtained by reacting $\text{Cu}(\text{pyr})_2$ with the appropriate amine taken in 1:1 molar ratio in boiling toluene.

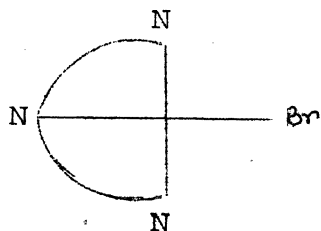


$\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ can be synthesised using the same procedure.

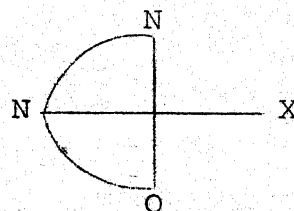
B. The Systems $\text{M}(\text{pyrenNR}_2)\text{Br}$ and $\text{M}(\text{pyrtnNR}_2)\text{Br}$

Physical data are set out in Tables II.1 - II.3. Representative electronic and infrared spectra are displayed in Figs. II.1 and II.2.

The nickel(II) system is diamagnetic while the copper(II) complexes have the normal magnetic moment of ~ 1.8 BM (Table II.1). These results suggest the structure VII. The most



(VII)



(VIII)

TABLE II.1

MAGNETIC SUSCEPTIBILITY DATA FOR $M(\text{pyrenNR}_2)\text{Br}$
and $M(\text{pyrtnNR}_2)\text{Br}$ COMPLEXES

Compound	Temp. °C	Susceptibility ^a		
		$\chi_g \times 10^6$	$\chi_M \times 10^6$	$\mu_{\text{eff}}(\text{BM})$
$\text{Cu}(\text{pyrenNEt}_2)\text{Br}$	30	3.46	1321	1.80
$\text{Cu}(\text{pyrtnNMe}_2)\text{Br}$	29	3.86	1387	1.84
$\text{Ni}(\text{pyrenNMe}_2)\text{Br}$	28			Diamagnetic
$\text{Ni}(\text{pyrenNEt}_2)\text{Br}$	28			Diamagnetic

a χ_g and χ_M are gram and corrected molar susceptibilities respectively in the solid state.

important point to note here is that both the ligand systems pyrenNR_2 and pyrtnNR_2 act in the tridentate fashion.

Analogous systems ($M(\text{tridentate})(\text{monodentate})$) derived from some other ligands are reported in literature.^{5,6-11} The properties of the present copper(II) systems are very much alike to those of salicylaldehyde systems of the type $\text{Cu}(\text{salenNR}_2)_X$ with coordination sphere VIII studied by us⁵ and others.⁶ Both systems show a prominent d-d band (Fig. II.1; Table II.3) in the region 670-600 nm. Interestingly the intensity of this band is higher in VIII (300-400) than in VII (~ 150). This may partly be due to lower symmetry of the coordination sphere VIII. Both $\text{Cu}(\text{pyrenNR}_2)\text{Br}$ and $\text{Cu}(\text{pyrtnNR}_2)\text{Br}$ show an intense band in the near ultraviolet (370 nm) (Table II.3 and Fig. II.1). This, and an additional band at 320 nm is also shown by the nickel species. No specific assignments have been made to these bands which may be of intraligand or metal-ligand origin. The electrical conductivity data (Table II.2) suggest that the compounds undergo partial dissociation (for complete dissociation, the conductivity¹¹ would be $75-95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in solution, probably via reactions of the type:

TABLE II.2

SELECTED INFRARED FREQUENCIES (cm^{-1}) AND ELECTRICAL CONDUCTIVITY^a
OF $\text{M}(\text{pyrenNR}_2)\text{Br}$ and $\text{M}(\text{pyrtnNR}_2)\text{Br}$ COMPLEXES

Compound	Phase	Assignment $\nu_{\text{C=N}}$	Electrical conductivity in nitromethane $\Lambda (\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1})$
$\text{Cu}(\text{pyrenNET}_2)\text{Br}$	KBr	1590	15
$\text{Cu}(\text{pyrtnNMe}_2)\text{Br}$	Nujol mull	1610	34
$\text{Ni}(\text{pyrenNMe}_2)\text{Br}$	Nujol mull	1585	15
$\text{Ni}(\text{pyrenNET}_2)\text{Br}$	Nujol mull	1590	19

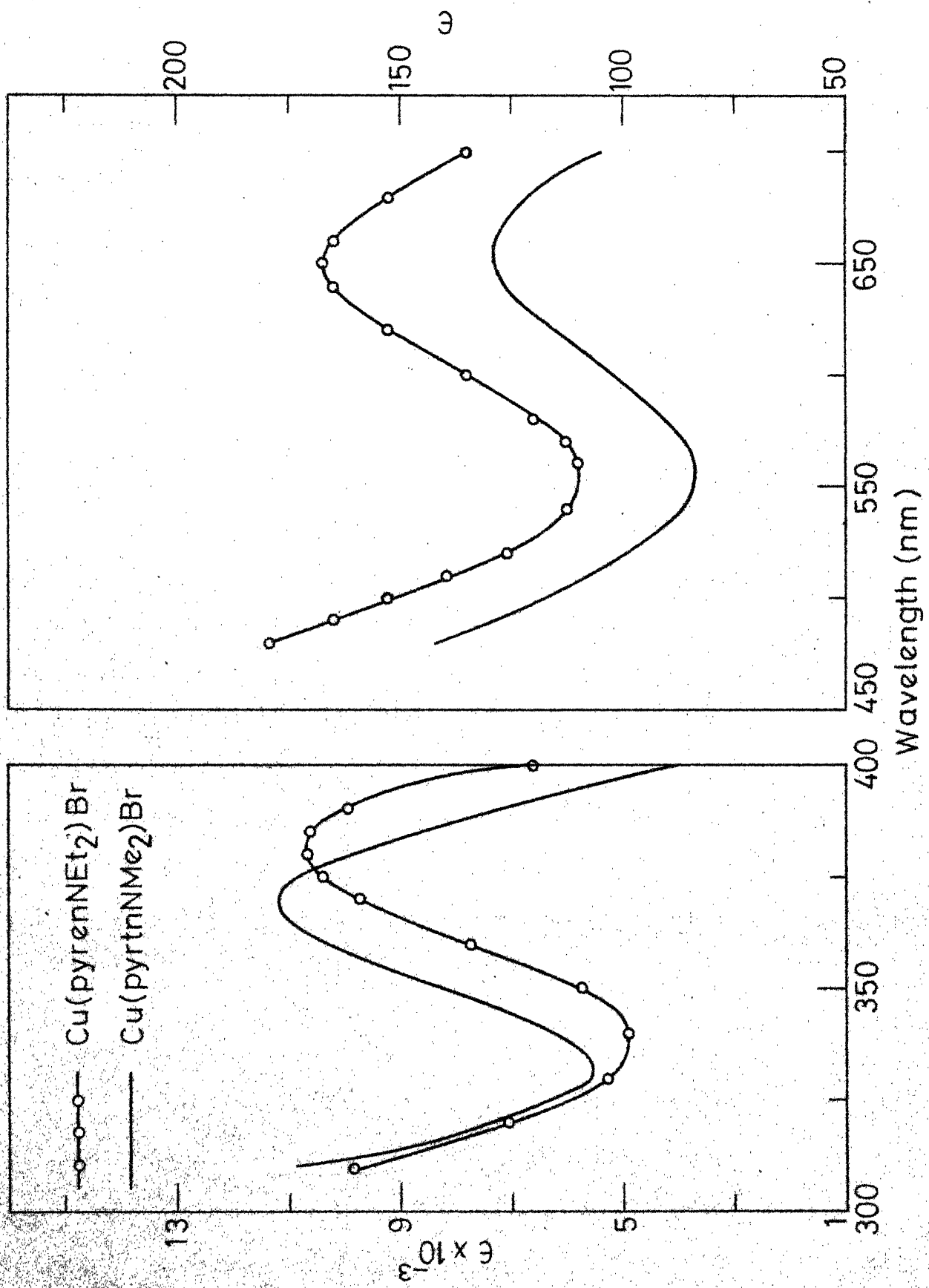
^a Measurements were made at 28°C and solute concentrations were in the range $1\text{--}3 \times 10^{-3}$ M.

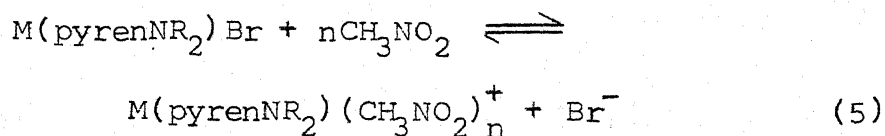
TABLE II.3

ABSORPTION MAXIMA (λ , nm) AND EXTINCTION COEFFICIENTS^a (ϵ , L.MOL⁻¹.CM⁻¹) OF ELECTRONIC BANDS OF M(pyrenNR₂)Br AND M(pyrtnNR₂)Br COMPLEXES AT ROOM TEMPERATURE (25-30°C)

Compound	Medium	λ (ϵ)
Cu(pyrenNEt ₂)Br	Nujol mull	620, 520sh, 410
	Toluene	650(168), 500sh(153), 380(10693)
Cu(pyrtnNMe ₂)Br	Nujol mull	650, 530sh, 415
	Toluene	655(135), 360(11173)
Ni(pyrenNMe ₂)Br	Nujol mull	620sh, 425
	Toluene	580sh(178), 420(4086), 370(4917), 320(9072)
Ni(pyrenNEt ₂)Br	Nujol mull	620sh, 410
	Toluene	580sh(166), 425(5371), 370(4297), 320(7213)

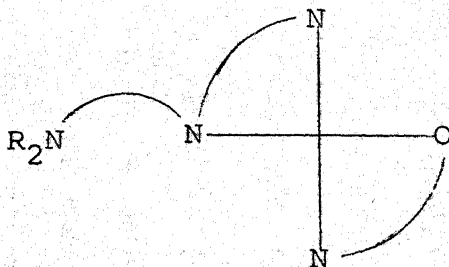
^a Solute concentrations were adjusted (between $2-3 \times 10^{-3}$ M) so as to get the optical density value in the range 0.5-1; sh is shoulder.





C. Cu(pyr)(pyrenNR₂) System

Physical data are set out in Tables II.4 - II.6. We shall briefly consider the infrared results (Table II.4, Fig. II.2) first. Cu(pyr)₂ shows the C=O stretch at 1650 cm⁻¹, while the Cu(tridentate)Br system described earlier, has the C=N stretch at ~1600 cm⁻¹ (Table II.2). As expected, the mixed ligand complexes show both C=O and C=N stretches. Cu(pyr)(pyrenNEt₂) was found to be monomolecular in freezing benzene (Mol. Wt. Found: 362; Calcd: 350). The complexes could be either pentacoordinated belonging to the class M(bidentate)(tridentate) with all potential donor sites bound to the metal or tetraordinated and planar with bidentate pyrenNR₂ as in IX. (NR₂ group is not coordinated to the metal). The systems have normal magnetic moments (Table II.5), which are of no diagnostic value for structural identification. Ligand field spectra however, throw some light on this problem. Usually pentacoordinated copper(II)



(IX)

TABLE II.4

SELECTED INFRARED FREQUENCIES (cm^{-1}) OF $\text{M}(\text{pyr})(\text{pyrenNR}_2)$
AND $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ COMPLEXES

Compound	Phase	Assignment	
		ν C=O	ν C=N
$\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$	Nujol	1615	1595
$\text{Cu}(\text{pyr})(\text{pyrenNEt}_2)$	Nujol	1613	1598
$\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$	Nujol	1640	1585
$\text{Cu}(\text{pyr})(\text{pyrtnNMe}_2)$	Nujol	1610	1590
$\text{Cu}(\text{pyr})(\text{pyrtnNEt}_2)$	Nujol	1605	1595

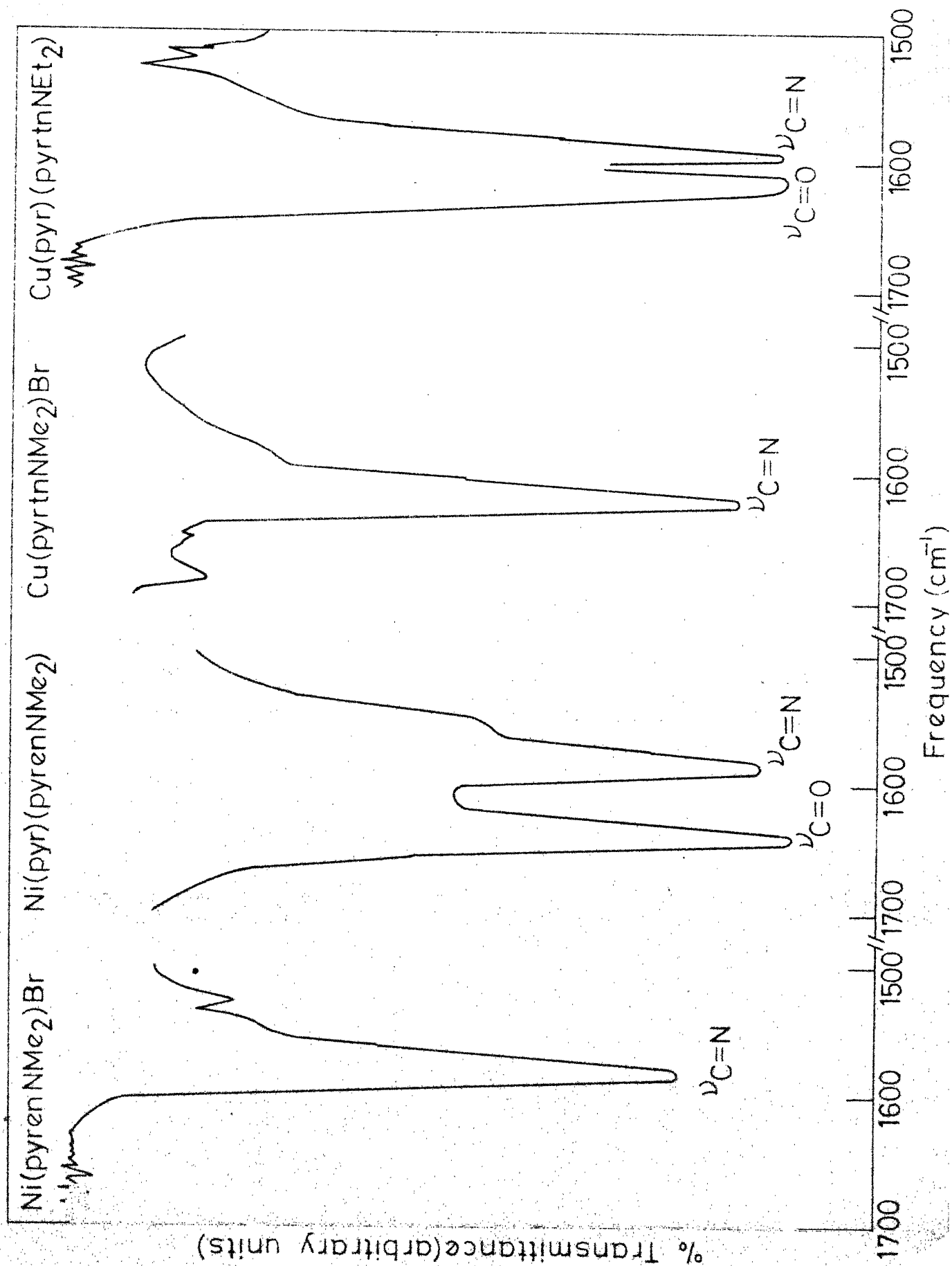


TABLE II.5

MAGNETIC SUSCEPTIBILITY^a DATA FOR M(Pyr)(pyrenNR₂)
AND Cu(pyr)(pyrtnNR₂) COMPLEXES

Compound	Temp. °C	$\chi_g \times 10^6$	$\chi_M \times 10^6$	μ_{eff} (BM)
Cu(pyr)(pyrenNMe ₂)	32	3.97	1427	1.88
Cu(pyr)(pyrenNEt ₂)	32	3.68	1421	1.88
Ni(pyr)(pyrenNMe ₂)			Diamagnetic	
Cu(pyr)(pyrtnNMe ₂)	32	3.82	1445	1.88
Cu(pyr)(pyrtnNEt ₂)	32	3.88	1598	1.98

^a χ_g and χ_M are gram and corrected molar susceptibilities respectively in the solid state.

species give rise to two bands in the visible region^{12,13} (*vide supra*). $\text{Cu}(\text{pyr})(\text{pyrenNR}_2)$ shows only one band around 600 nm (Table II.6; Fig. II.3). The planar complex¹⁴ $\text{Cu}(\text{pyr})_2$ having the $\text{Cu}_2\text{N}_2\text{O}_2$ chromophore shows a single broad ligand field transition centred at 650 nm. On the other hand complexes of the type V with planar CuN_4 coordination sphere show² the corresponding transition around 550 nm. The structural type IX has CuN_3O coordination sphere and may be expected to give rise to a ligand field band in the intermediate range namely 650-550 nm. This is in line with experimental observation.

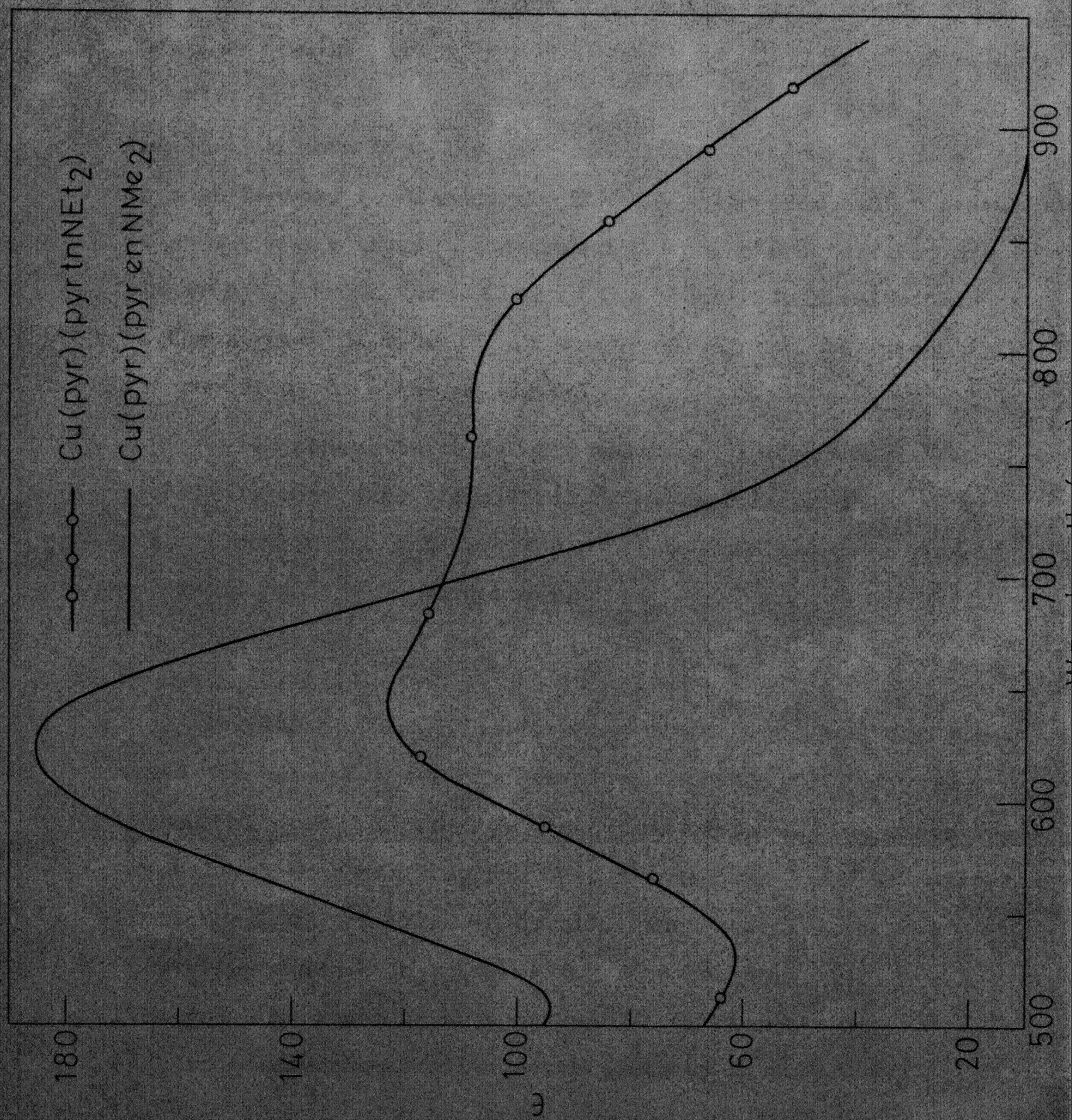
Infrared data throw some additional light supporting the structure IX. Infrared data were collected on the complex $\text{Cu}(\text{pyr})(\text{pyrNHet})$ in which substituents on the amine nitrogen of the tridentate moiety are H and Et. This complex was synthesised with the hope that N-H frequency will give us an idea about whether the terminal nitrogen is coordinated or not. The N-H stretching frequencies in secondary amines and imines fall¹⁴ in the range $3300\text{--}3500\text{ cm}^{-1}$ in the absence of molecular association. The complex $\text{Cu}(\text{pyr})(\text{pyrNHet})$ gives rise to a band at 3310 cm^{-1} in dichloroethane. The N-H frequency is thus not much influenced. This is an indication that NHet nitrogen is not coordinated to the metal. In many salicylaldehyde complexes where an NHR group is coordinated to a metal a lowering of the N-H stretching frequency by $\sim 200\text{ cm}^{-1}$ is often observed.^{5,6,15}

TABLE II.6

ABSORPTION MAXIMA (λ , nm) AND EXTINCTION COEFFICIENTS^a (ϵ , L.MOL⁻¹.CM⁻¹) OF ELECTRONIC BANDS OF M(pyr)(pyrenNR₂) AND Cu(pyr)(pyrtnNR₂) COMPLEXES

Compound	Medium	$\lambda(\epsilon)$
Cu(pyr)(pyrenNMe ₂)	Nujol mull	580
	Benzene	620(186)
Cu(pyr)(pyrenNEt ₂)	Nujol mull	590
	Benzene	640(205)
Ni(pyr)(pyrenNMe ₂)	Nujol mull	415sh
	Benzene	410sh(176)
Cu(pyr)(pyrtnNMe ₂)	Nujol mull	565
	Benzene	790(105), 630(135)
Cu(pyr)(pyrtnNEt ₂)	Nujol mull	800, 625
	Benzene	790(108), 640(123)

^a Solute concentrations were adjusted (between $2-3 \times 10^{-3}$ M) so as to get the optical density value in the range 0.5-1; sh is shoulder.



D. Ni(pyr)(pyrenNMe₂)

More definitive evidence in favour of structure IX is obtained from studies of mixed crystals of Cu(pyr)(pyrenNMe₂) and Ni(pyr)(pyrenNMe₂). Before we proceed to describe these results, we note that the pure nickel(II) complex is monomeric in solution and is diamagnetic both in solid phase and in solution. It shows an electronic band around 410 nm, characteristic of planar NiN₄ chromophore. Clearly the nickel(II) species belongs to the structural type IX, in which the NR₂ (R = Me) group is not coordinated to the metal ion.

X-ray powder patterns were taken on pure copper(II) and nickel(II) complexes (Fig. II.4). The calculated d-spacings are set out in Table II.7. The two pure complexes are clearly not isomorphous with each other.

E. Mixed Crystals

In spite of lack of isomorphism of the two pure complexes, mixed crystals of the two containing more than 50% Cu(pyr)-(pyrenNMe₂) could be readily grown from benzene. One mixed crystal system containing 56% Cu(pyr)(pyrenNMe₂) and 44% Ni(pyr)-(pyrenNMe₂) was examined in detail. The magnetic moment of Cu(pyr)(pyrenNMe₂) in this was found to be normal viz., 1.84 ± 0.1 BM assuming that nickel(II) is diamagnetic. The electronic spectrum of mixed crystal taken in nujol mull is fully in accord. The spectrum shows a band at 600 nm

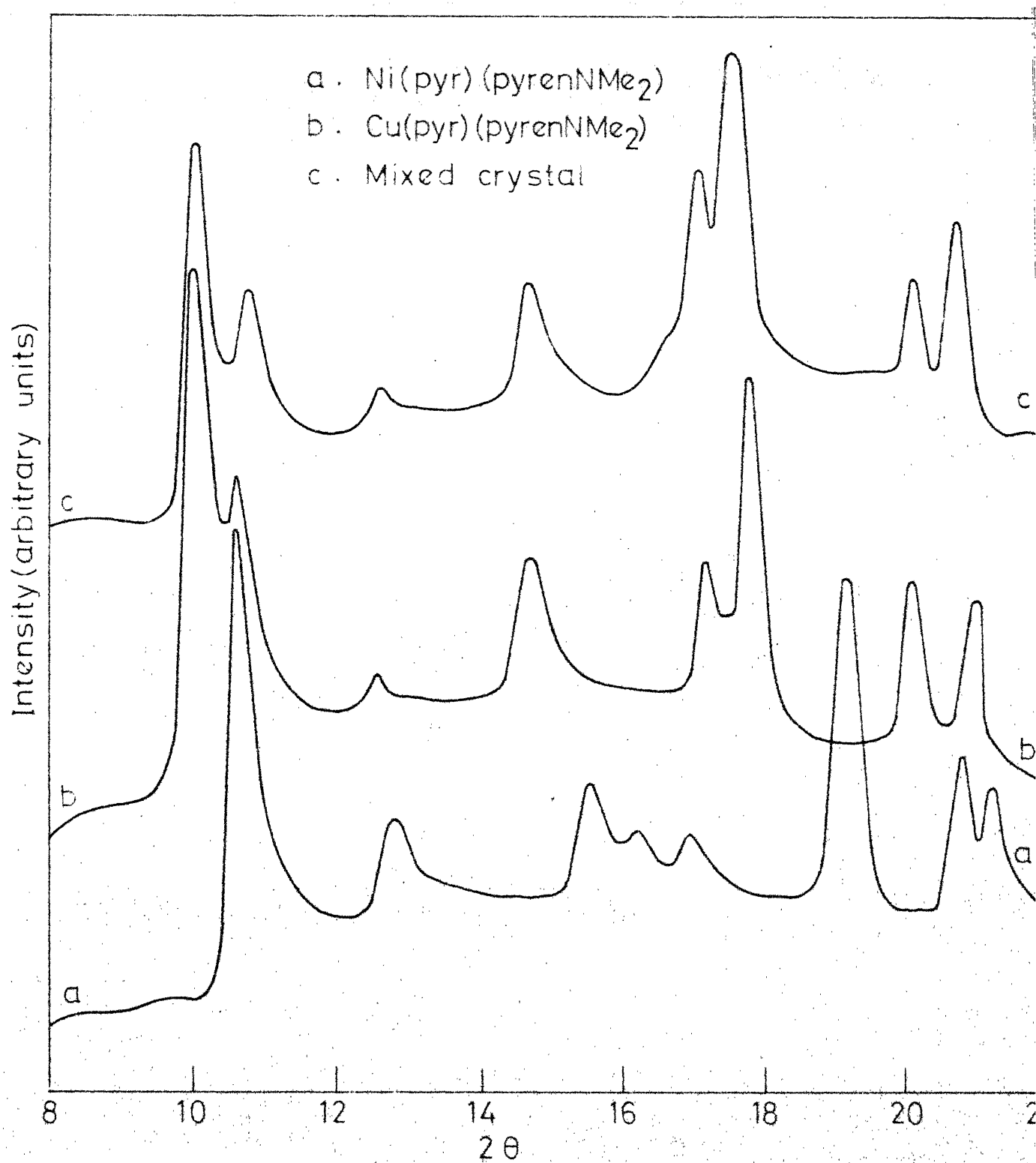


FIG. II.4 X-RAY POWDER PATTERNS OF $M(\text{pyr})(\text{pyrenNR}_2)$ COMPLEXES

TABLE II.7

X-RAY POWDER PATTERN DATA^a OF M(pyr)(pyrenNR₂) COMPLEXES

Ni(pyr)(pyrenNMe ₂)		Cu(pyr)(pyrenNMe ₂)		Mixed crystal	
2θ	d-spacings	2θ	d-spacings	2θ	d-spacings
10.5	8.43	10.0	8.84	10.05	8.82
12.8	6.92	10.6	8.35	10.8	8.19
15.5	5.72	12.6	7.03	12.6	7.03
16.2	5.47	14.7	6.03	14.7	6.03
16.9	5.25	17.2	5.16	17.0	5.22
19.15	4.63	17.8	4.98	17.6	5.04
20.8	4.27	20.1	4.42	20.1	4.42
21.1	4.21	20.85	4.26	20.7	4.29

^a The first eight reflections with 2θ in the range 10-21° are reported.

characteristic of copper(II) species and a shoulder around 420 nm due to the planar nickel(II) species (compare with results of Table II.6).

The most important observation is that the mixed crystals are isomorphous with pure $\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$, as determined from X-ray powder patterns and d-spacings (Table II.7; Fig. II.4). Since nickel(II) is diamagnetic and planar (IX) in the mixed crystal, it follows that the copper(II) species has also the geometry IX in the mixed crystal. Because of isomorphism, this is also true for the pure copper(II) complex. We thus conclude that $\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$ has the planar environment IX. The lack of isomorphism of pure copper(II) and nickel(II) complexes must arise from different packing of otherwise structurally very similar molecules.

The epr spectrum of a very dilute solution of $\text{Cu}(\text{pyr})-(\text{pyrenNMe}_2)$ in $\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$ (such solutions have of course the structure of the latter pure complex) was examined in the powder form at room temperature. The spectrum is displayed in Fig. II.5. This is an axial spectrum with a so-called extra line^{15a,15b} in the perpendicular region. A spectrum computer-simulated with parameters

$$g_{\parallel} = 2.199 ; \quad A_{\parallel} = 187.0 \text{ Gauss}$$

$$g_{\perp} = 2.045 ; \quad A_{\perp} = 6.0 \text{ Gauss.}$$

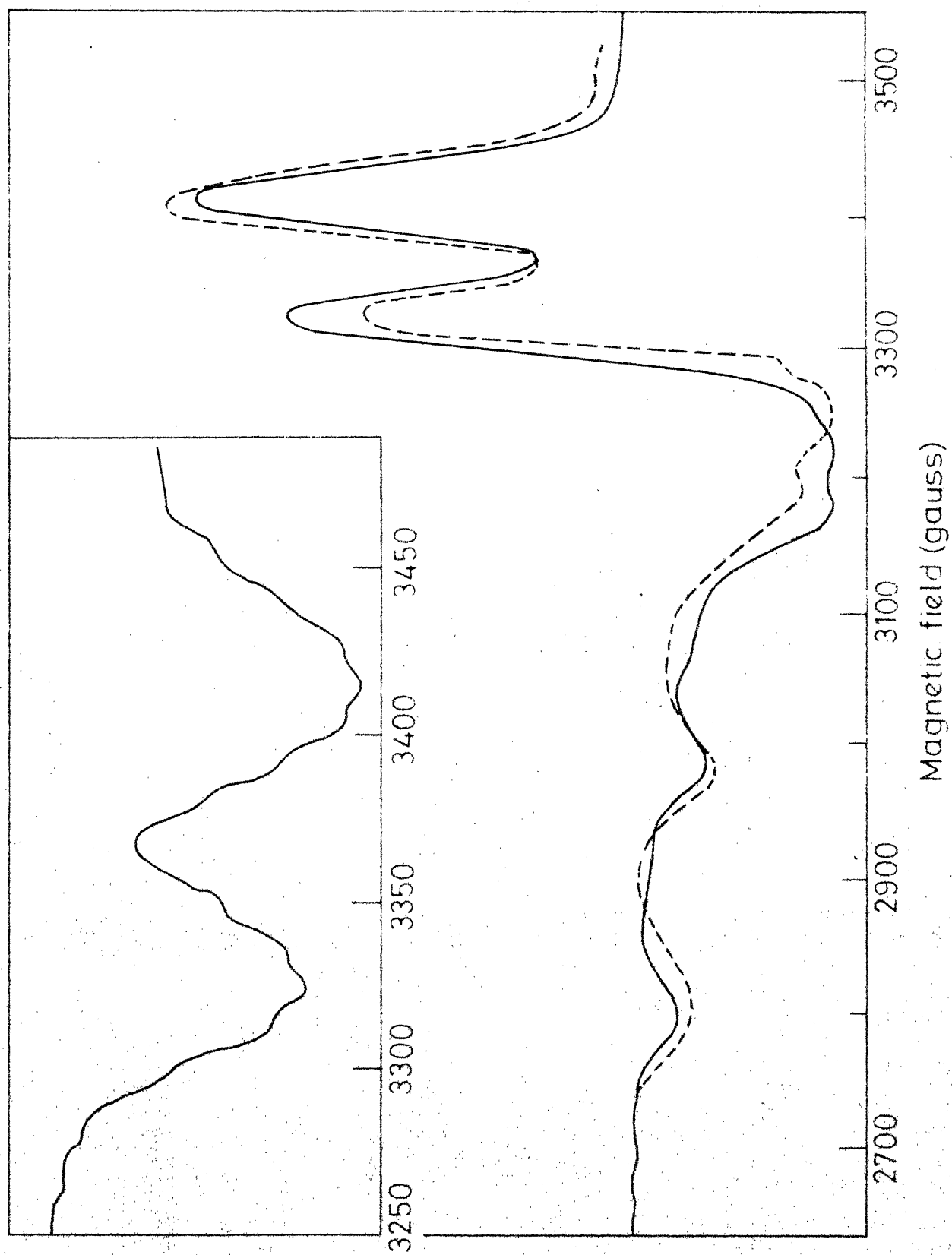


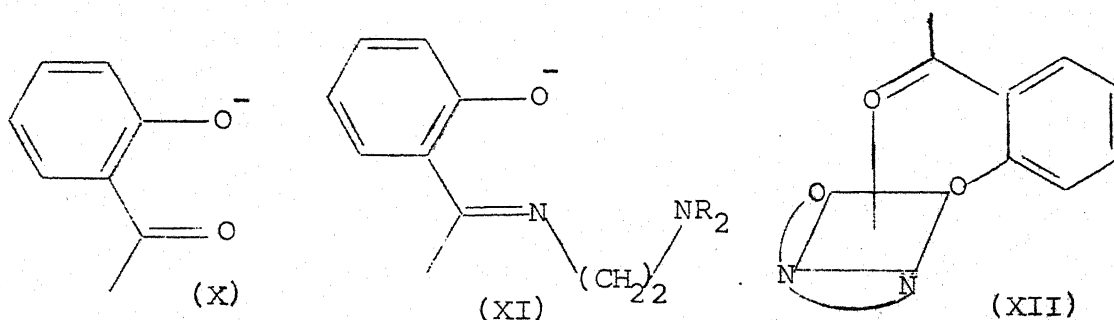
FIG. II.5 POWDER EPR SPECTRA OF MIXED CRYSTAL. OBSERVED SPECTRUM(—);

fits very well with the experimental spectrum (Fig. II.5). The width of Lorentzian lines (of which the observed is an envelope) were taken as 50G and 40G for parallel and perpendicular regions respectively. I am thankful to Mr. S. Baral of this laboratory for his assistance in Computer simulation. Rich superhyperfine splittings are observed in expanded spectra in the perpendicular (but not in the parallel) region (inset in Fig. II.5) due the existence of spin density on nitrogen binding sites and possibly adjacent hydrogen atoms.^{15c} No further analysis of the superhyperfine structure was made. We hope to do so from single crystal epr data which are now being collected.

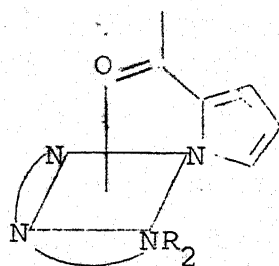
In Chapter I (Section I.2), we have categorised the various ways in which pentacoordination may be hindered in a M(bidentate)(tridentate) system. The pyrrole-2-alimine species described above, provides an example where the potentially tridentate unit, actually acts only as a bidentate ligand (vide structure III, Chapter I). In the next section, we examine why this happens so.

F. Steric Factors

It is firmly established^{5,16} that $\text{Cu}(\text{sal})(\text{salenNR}_2)(\text{X}, \text{sal}; \text{XI}, \text{salenNR}_2)$ has the square pyramidal structure XII. In view of this and in view of the observation that in $\text{M}(\text{pyrenNR}_2)$, pyrenNR_2 is tridentate, it is pertinent to examine why pyrenNR_2 fails to use NR_2 coordination in $\text{M}(\text{pyr})(\text{pyrenNR}_2)$. We strongly



suspect that the phenomenon is of steric origin. Like salenNR₂ in XII and other structures,¹⁷ pyrenNR₂ in its tridentate mode will be able to span only in the meridional fashion due to the short length of the -(CH₂)₂- chain. Models show that this brings the bidentate pyr moiety unfavourably close to the methyl groups of NMe₂ in pyrenNMe₂ in the hypothetical square pyramidal structure XIII:

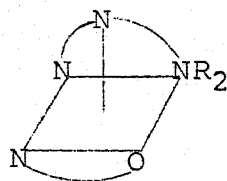


(XIII)

This steric hindrance leads to the delinking of NMe₂ from the metal atom. In XII, the benzene ring of sal is situated one bond (O-C) away from the corner of the basal plane and also the chelate ring is six-membered. Models clearly demonstrate that steric interaction between sal and NR₂ is virtually absent.

G. Pentacoordination in $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$

If the above thesis regarding the steric effect in $\text{M}(\text{pyr})-(\text{pyrenNR}_2)$ is correct, the complexes $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ with a more flexible $-(\text{CH}_2)_3-$ chain may be pentacoordinated. In this potentially tridentate ligand can span facially. Models show that the configuration XIV is free from steric strain:



(XIV)

With the above ideas in mind these complexes were synthesised by using methods analogous to those used for $\text{Cu}(\text{pyr})(\text{pyrenNR}_2)$. The complex $\text{Cu}(\text{pyr})(\text{pyrtnNET}_2)$ was found to be monomolecular in freezing benzene (Mol. wt., Found: 369; Calcd: 364). They have normal magnetic moments and infrared spectra (Table II.5 and II.3), and two distinct electronic bands in visible region (Fig. II.3). This spectrum is very much alike to that of $\text{Cu}(\text{sal})(\text{salenNR}_2)$ system.⁵ It is thus strongly suggestive of pentacoordination. In idealised C_{4v} geometry, the d-orbital order¹³ is $d_{xz,yz} < d_{xy} \sim d_{z^2} \ll d_{x^2-y^2}$. The two observed bands can be assigned as $d_{xy}, d_{z^2} \rightarrow d_{x^2-y^2}$, 790 nm; $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ 640 nm. Interestingly, the spectrum of $\text{Cu}(\text{pyr})(\text{pyrtnNMe}_2)$ in the solid state (one band 565 nm) (Fig. II.6) is very different

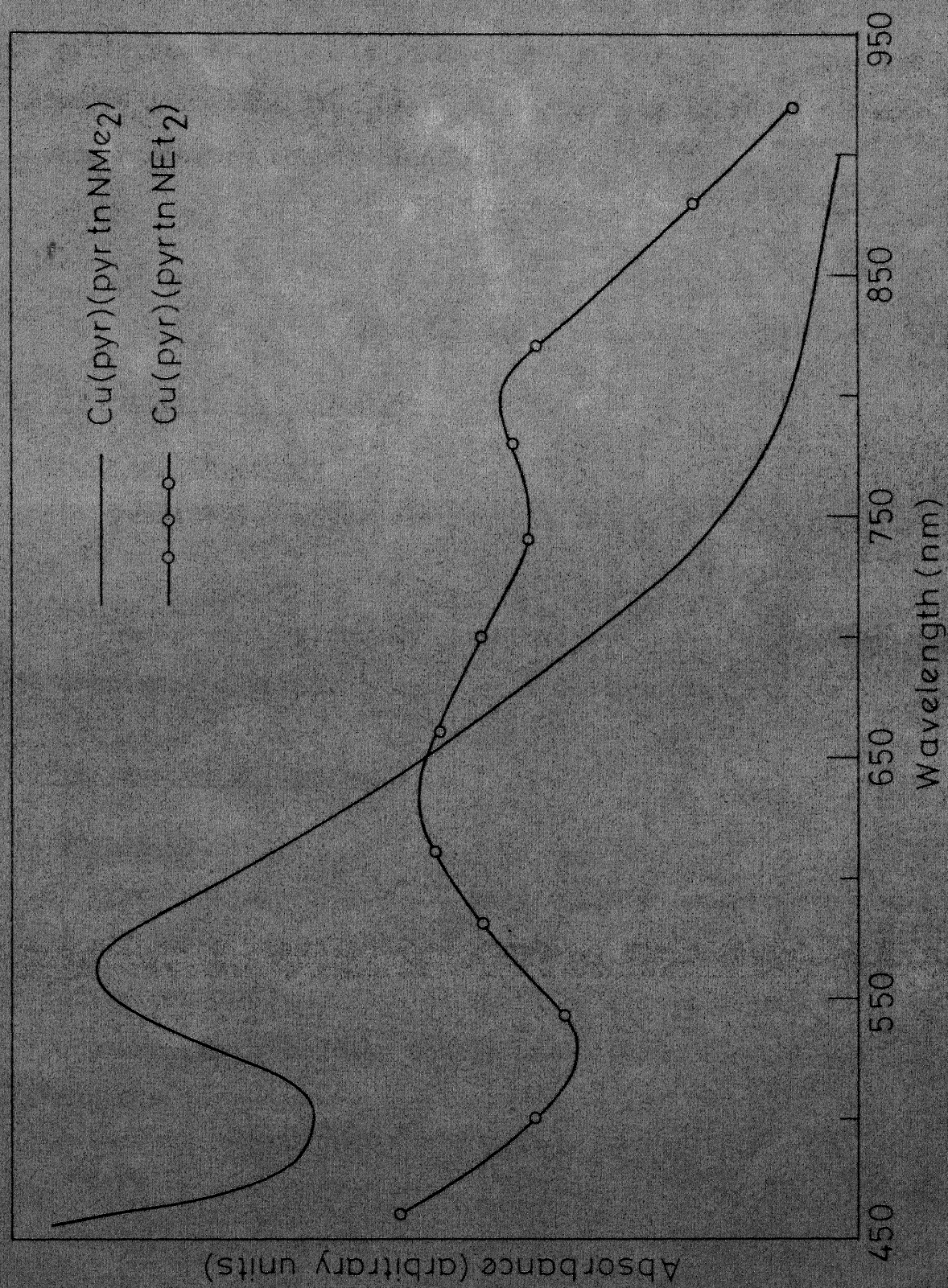


FIG. II.6 ELECTRONIC SPECTRA IN NUJOL MULL

from that in solution but is closely akin to the spectrum of $\text{Cu}(\text{pyr})(\text{pyrenNR}_2)$ (Table II.6). The former complex thus provides an important link being planar in the solid state and pentacoordinated in solution.

II.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Starting Chemicals

Pyrrole-2-aldehyde was synthesised as described in literature.¹⁸

The N,N-dialkylethylenediamines and N,N-dialkylpropylenediamines were obtained from Aldrich Chemical Co., U.S.A.

b. Preparation of Complexes

i. Schiff Bases

Pyrrole-2-aldehyde (0.01 mol) and the appropriate amine (0.01 mol) were taken in 20 ml ethanol. The solution was heated to reflux for 0.5 hr. Alcohol was then stripped on a rotary evaporator. The resulting Schiff base (brown liquid) was used without further purification.

ii. $\text{Cu}(\text{pyr})_2$

$\text{Cu}(\text{pyr})_2$ was prepared from pyrrole-2-aldehyde and basic carbonate of Cu(II) as described in literature.⁴

iii. M(pyrenNR₂)Br and M(pyrtnNR₂)Br

To a solution of Schiff base (0.01 mol) in 40 ml dry tetrahydrofuran, was added potassium t-butoxide (0.01 mol) followed by (Et₄N)₂MBr₄ (0.01 mol). The mixture was magnetically stirred for about 6 hr. During this period the solution became dark brown (M = Ni) or dark green (M = Cu). This was filtered and the residue was extracted several times with toluene. The toluene extract on concentrating gave dark coloured crystals. These were recrystallised from toluene. The yield was 50%.

iv. Cu(pyr)(pyrenNR₂) by Aqueous Reaction

Excess of appropriate amine was added to 0.02 mol of pyrrole-2-aldehyde and 0.01 mol of CuSO₄·5H₂O dissolved in 50 ml water. The solution was heated on a steam bath. After cooling to room temperature, 2 ml of 5% NaOH was added.

In the case of Cu(pyr)(pyrenNMe₂), the precipitated material was filtered and then extracted with ethanol-dichloromethane mixture. The extract was concentrated and cooled. Dark green crystals thus obtained were collected by filtration and recrystallised from dichloromethane.

In the case of Cu(pyr)(pyrenNEt₂) a green substance started depositing on the walls of the reaction vessel. When deposition was complete the aqueous portion was removed by decantation. The residue was dissolved in benzene and was dried over anhydrous sodium sulphate. The solution was then concentrated and hexane

was added. A gum separated. On standing for several days in air, the gum slowly transformed to microcrystals of the required complex. They were collected by filtration and were washed by hexane. The yield was 35%.

v. $\text{Cu}(\text{pyr})(\text{pyrenNR}_2)$ and $\text{Cu}(\text{pyr})(\text{pyrenNHEt})$ in Nonaqueous Medium

0.02 mol of $\text{Cu}(\text{pyr})_2$ and 0.02 mol of the appropriate amine were taken in 40 ml of toluene and the mixture was heated to reflux for 1 hr. The mixture was then filtered and its volume was reduced to 10 ml. 10 ml of hexane was then added. Green crystals separated out on cooling. These were collected by filtration and recrystallised from toluene-hexane mixture. The synthesis in non-aqueous medium is more convenient than the synthesis in aqueous medium.

vi. $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$

These were prepared by procedures similar to those used for $\text{Cu}(\text{pyr})(\text{pyrenNR}_2)$.

vii. $\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$

A nonaqueous chelation reaction of pyrrole-2-aldehyde (0.01 mol), pyrenNMe_2 (0.01 mol), potassium-t-butoxide (0.02 mol) and $(\text{Et}_4\text{N})_2\text{NiBr}_4$ (0.01 mol) in tetrahydrofuran using a procedure entirely analogous to that used for $(\text{M}(\text{pyrenNR}_2)\text{Br})$ gave dark brown crystals of composition $\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$.

viii. Mixed Crystal

The mixed crystals were prepared as follows. A benzene solutions of $\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$ (0.01 mol) and $\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$ (0.01 mol) were mixed. This was heated on steam bath. Slow evaporation of the solution yielded dark coloured mixed crystals.

The composition of the crystals were determined using the band intensity at 620 nm (Table II.6) as an index of the concentration of the copper(II) complex. The mixed crystals were found to have 56% $\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$ and 44% $\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$. The yield was 50%.

B. Characterization of Complexes

a. C, H, N Analyses

These were done by microanalytical methods. Characterization data for all complexes are collected in Table II.8.

b. Gravimetric Estimation of Copper

The complexes were decomposed by heating with concentrated HNO_3 (5 ml) and then with concentrated HCl till the brown fumes ceased to appear. After cooling, 50 ml of water was added and the solution was neutralised with 5% NaOH till a little of white precipitate formed. To this 1 ml of conc. H_2SO_4 and 15 ml of 5% sodium bisulphite solution were added. The solution was heated nearly to boiling and 10 ml of 10% NH_4SCN

TABLE II.8

CHARACTERIZATION DATA FOR $M(\text{pyrenNR}_2)\text{Br}$, $M(\text{pyrtnNR}_2)\text{Br}$,
 $M(\text{pyr})(\text{pyrenNR}_2)$ and $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ COMPLEXES

Compound	Mp, °C ^a	%C		%H		%N		%M ^b	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$\text{Cu}(\text{pyrenNEt}_2)\text{Br}$	127-128	39.34	39.50	5.41	5.56	12.56	12.30	18.91	18.77
$\text{Cu}(\text{pyrenNMe}_2)\text{Br}$	150-151	37.32	37.35	5.01	5.12	13.11	12.80	19.74	19.59
$\text{Ni}(\text{pyrenNMe}_2)\text{Br}$	216-217	35.67	35.22	4.66	4.31	13.92	13.80	19.37	19.50
$\text{Ni}(\text{pyrenNEt}_2)\text{Br}$	141-142	39.92	39.73	5.49	5.58	12.74	12.70	17.72	17.85
$\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$	157-158	52.24	52.36	5.64	6.00	17.41	17.30	19.74	19.79
$\text{Cu}(\text{pyr})(\text{pyrenNEt}_2)$	112-113	54.92	54.99	6.34	6.53	16.01	15.97	18.16	17.95
$\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$	189-190	53.00	53.02	5.72	5.80	17.73	17.60	18.51	18.50
$\text{Cu}(\text{pyr})(\text{pyrtnNMe}_2)$	180-181	53.64	53.75	6.00	5.84	16.68	16.88	18.92	18.97
$\text{Cu}(\text{pyr})(\text{pyrtnNEt}_2)$	113-114	56.10	56.35	6.65	6.75	15.39	15.53	17.46	17.46

^a All melting points are uncorrected.

^b Copper was estimated as CuSCN and nickel as dimethylglyoximate.

solution was added with stirring. It was allowed to stand for 4 hr. after which it was filtered through G-4 sintered crucible. The residue was dried at 110°C and weighed as CuSCN .

c. Gravimetric Estimation of Nickel

Accurately weighed (100 mg) compound was taken in a conical flask. It was decomposed by heating on a hot plate with conc. HNO_3 (twice with 5 ml portions) 10 ml of conc. HCl was added and the mixture was heated to boil till the brown fumes ceased to evolve being replaced by white fumes. After cooling to room temperature 15-20 ml of water was added. Usually some insoluble material separated out on the surface of the faint green solution which was then filtered through sintered funnel. The sintered funnel was given a repeated wash by distilled water. The volume of the filtrate and washings together increased to 100 ml. The solution was heated on a steam bath and slight excess of dimethylglyoxime (1% solution in 95% ethanol; calculated on the basis of 1 ml per 2 mg of nickel) was added. It was made alkaline with ammonia (a little in excess). The red precipitate was digested on steam bath for 2-3 hr. It was then filtered through a preweighed sintered crucible. The precipitate was washed with 20% ethanol till free from chloride. It was dried at $110-120^{\circ}\text{C}$ for 2 hr, cooled in a desiccator and weighed to constant weight as bis(dimethylglyoximato)nickel(II).

C. Solvents

Tetrahydrofuran was kept over fused calcium chloride for 12 hr. Then it was heated to reflux over sodium wire in presence of benzophenone till the colour became deep blue. It was distilled and used immediately. Benzene was purified by successive shaking with concentrated sulphuric acid (to remove thiophene), sodium bicarbonate solution and water. The solvent was then dried over fused calcium chloride and was finally distilled over sodium. Nitromethane was kept over anhydrous sodium sulphate and was distilled just before use. The middle fraction (boiling point 101°C) was collected. Toluene was distilled over sodium. Dichloromethane and other solvents required for recrystallisation were taken straight from bottles of British Drug House AnalaR quality or equivalent.

D. Physical Measurements

a. Infrared Spectra

These were recorded on a Perkin-Elmer 531 recording spectrophotometer either in nujol mull, as KBr. pellets or in solution.

b. Electronic Spectra

These were measured on a Cary-14 recording spectrophotometer. Solid samples were examined in finely dispersed hydrocarbon mulls sandwiched between quartz plates. Silica cells

of path length (1-2 cm) were used depending on the concentration of solutions and intensities of bands.

c. Molecular Weight

Molecular weights were determined in carefully purified benzene using the cryoscopic procedure in presence of sodium sulphate.¹⁹

d. Electrical Conductance Measurements

These were measured on a Systronics (India) conductivity bridge using a platinised conductivity cell with a cell constant $= 0.548 \text{ cm}^{-1}$.

e. Bulk Susceptibility Measurements

These were carried out using a sensitive Gouy balance²⁰ assembled by Dr. T.S. Kannan and Dr. S. Gupta of this laboratory. The unit consists of a Varian V-4005 electromagnet (pole caps tapered to one inch diameter) a matching V-2900 solid state power supply and an Ainsworth semimicro balance. The current fed to the magnet could be regulated to carry out variable field measurements. All measurements were carried out over a wide range of field strengths.

Split sample tubes were used for all measurements on solids. Either $\text{CoHg}(\text{SCN})_4$ ²¹ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used as the standard. From the observed weight differences, the susceptibility of the sample was calculated using standard equations.²²

The diamagnetic correction for the ligands and metal ion was made on the basis of Pascal's constants given by Selwood.²²

f. Magnetic Susceptibility of Mixed Crystal

The gram susceptibility (χ_g) observed for the mixed crystal can be written as

$$(\chi_g)_{mc} = f_{Cu}(\chi_g)_{Cu} + f_{Ni}(\chi_g)_{Ni} \quad (6)$$

where f_{Cu} and f_{Ni} are respectively the weight fraction of the copper(II) and nickel(II) complexes and $(\chi_g)_{Cu}$ and $(\chi_g)_{Ni}$ are the respective gram susceptibilities. We have $f_{Cu} = 0.56$; $f_{Ni} = 0.44$; $(\chi_g)_{Ni} = 0.47 \times 10^{-6}$ cgs units (calculated from Pascal's constants). $(\chi_g)_{mc}$ is found to be 2.04×10^{-6} cgs units. Using Eqn. (6) we get $(\chi_g)_{Cu} = 4.00 \times 10^{-6}$ cgs units and hence $(\chi_M)_{Cu}$ (corrected for diamagnetism) = 1437. This yields μ_{eff} for copper(II) in the mixed crystal as 1.84 BM.

g. X-Ray Powder Pattern

These data were collected on a GE XRD-6 Diffractometer with $CuK\alpha$ radiation.

h. Electron Spin Resonance Spectra

The powder epr spectra were recorded on a Varian V-4502 EPR Spectrometer operating at the X-band frequency (9.5 GHz). The Zeeman field at the site of the sample inside the cavity was modulated by 100 KHz frequency modulation. Diphenylpicrylhydrazyl (DPPH) ($g = 2.0036$) was used as the standard field marker.

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CHAPTER III

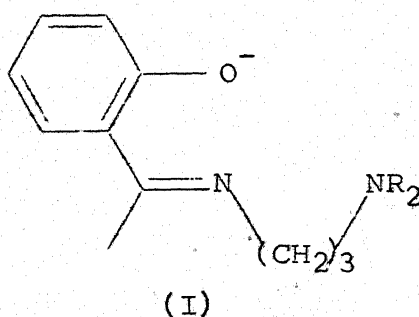
DIMERIC MIXED COMPLEXES WITH NICKEL(II)*

Abstract: By reacting trimeric bis-(acetylacetonato)nickel(II) with tridentate Schiff bases derived from salicylaldehyde and N,N-dialkyl-1,3-diaminopropylenediamine, new dinuclear mixed ligand species of the type $\text{Ni}_2(\text{bidentate})_3(\text{tridentate})$ have been obtained. The probable structure of such species is described on the basis of various physicochemical data. Nickel(II) has octahedral environment in these complexes.

*The work described in this chapter has appeared in Ind. J. Chem., 14A, 785 (1976).

III.1 INTRODUCTION

In our search for the pentacoordinated species of the type $\text{Ni}(\text{bidentate})(\text{tridentate})$, the reaction of bis(acetylacetonato)nickel(II), $\text{Ni}_3(\text{ac})_6$ with HsalenNR_2 was investigated earlier (Chapter I). Square pyramidal species of the type $\text{Ni}(\text{ac})(\text{salenNR}_2)$ were thus obtained. Having observed the dramatic stereochemical consequence of the $-(\text{CH}_2)_n-$ chain length in pyrrole-2-alimine complexes (Chapter II), we undertook the investigation of the effect of this chain length on the composition and stereochemistry of some nickel(II) species. The systems obtained by reacting $\text{Ni}_3(\text{ac})_6$ with salenNR_2 (I) are reported in this chapter. The properties of the species obtained are compared with those of $\text{Ni}(\text{ac})(\text{salenNR}_2)$.



III.2 RESULTS AND DISCUSSION

A. Syntheses

Three Schiff bases of the type I were prepared ($R = \text{Me}$, Et , and Bu). By reacting the Schiff base (0.1 mol) with $\text{Ni}_3(\text{ac})_6$

(0.07 mol) in toluene green crystals of composition $\text{Ni}_2(\text{ac})_3^-$ (saltn NR_2) are readily obtained.

The observed molecular weights are in line with the above formulation (Table III.1).

B. Physical Data and Structure

All the complexes show an ir band (Fig. III.1 and Table III.1) in the region $1620\text{--}1630\text{ cm}^{-1}$ assigned to $\nu_{\text{C}=\text{N}}$ of the Schiff base moiety. There are two strong bands at 1590 cm^{-1} and 1510 cm^{-1} which are due to the combination of $\nu_{\text{C}\equiv\text{C}}$ and $\nu_{\text{C}\equiv\text{O}}$ stretches of ac with additional contributions from aromatic vibrations of the Schiff base.

The complexes are fully paramagnetic both in the solid state and in chloroform solution (Tables III.2 and III.3). In the visible region the complexes show two bands at 1170 nm and $\sim 640\text{ nm}$ (Fig. III.2 and Table III.4). The bands are weak and are clearly of ligand field origin. The spectrum suggests pseudooctahedral nickel(II) stereochemistry. The two bands can be readily assigned as: ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, 1170 nm; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, $\sim 640\text{ nm}$.

On the basis of model building it is proposed that $\text{Ni}_2(\text{ac})_3^-$ (saltn NR_2) has the structure II in which ac occupies bridging positions. It is known that the dinuclear fragment is coordinatively unsaturated and yields adducts such as ${}^2\text{Ni}_2(\text{ac})_4(\text{pyridine})$ in which nickel(II) is octahedral. One may then expect

TABLE III.1

SELECTED INFRARED FREQUENCIES (cm^{-1}) AND MOLECULAR WEIGHT DATA^a OF
 $\text{Ni}_2(\text{ac})_3(\text{saltnNR}_2)$ COMPLEXES

Compound	Assignment			Molecular weight	
	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}} + \nu_{\text{C}\equiv\text{C}} + \nu_{\text{aromatic}}$		Calcd	Found
$\text{Ni}_2(\text{ac})_3(\text{saltnNMe}_2)$	1623	1591, 1508		620	600
$\text{Ni}_2(\text{ac})_3(\text{saltnNEt}_2)$	1627	1591, 1509	^b		
$\text{Ni}_2(\text{ac})_3(\text{saltnNBu}_2)$	1628	1593, 1508		704	675

^a Molecular weights were determined cryoscopically in purified dry benzene.

^b Measurement not done.

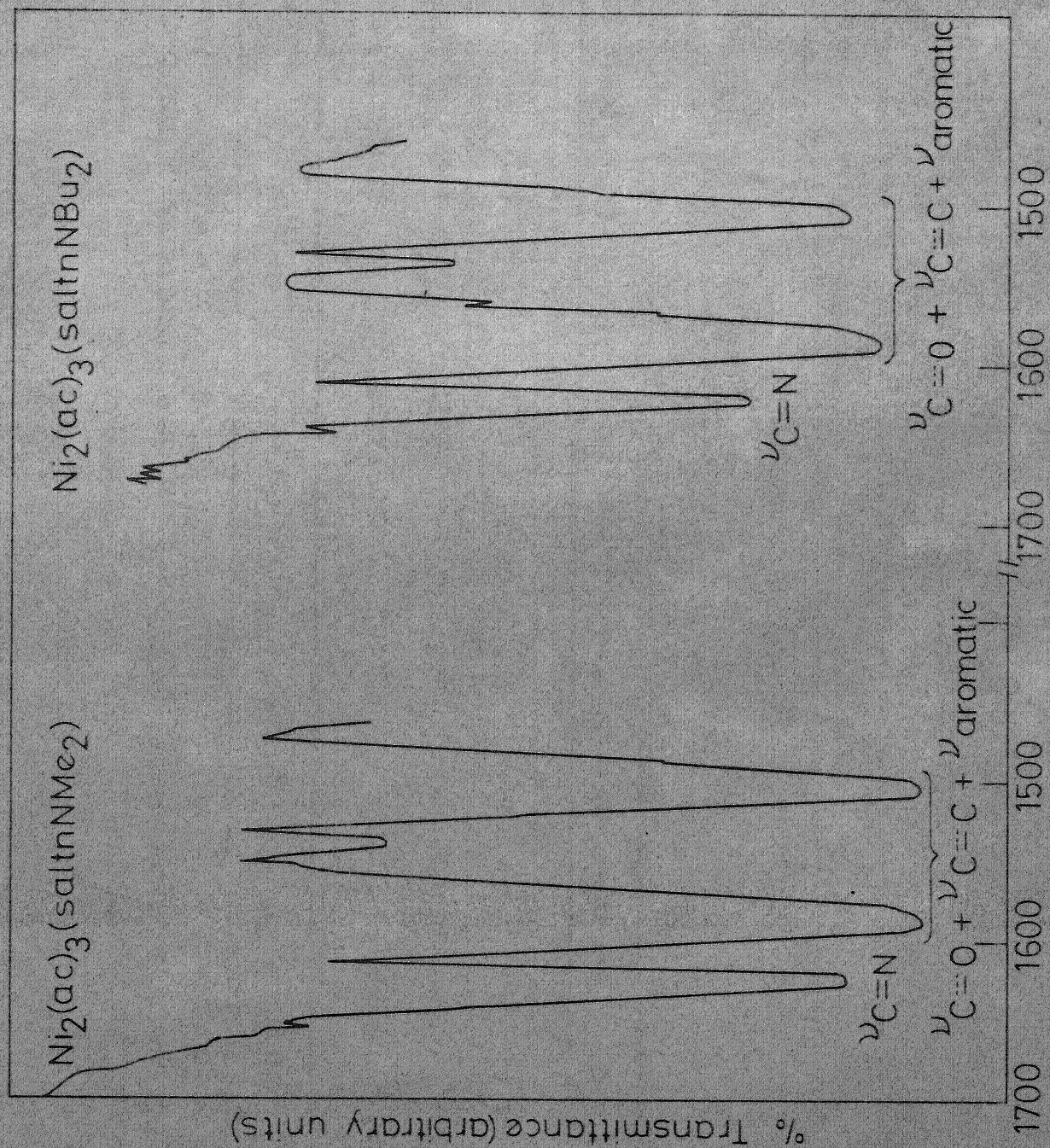
FIG. III.1 SELECTED INFRARED FREQUENCIES (cm^{-1})

TABLE III.2

MAGNETIC SUSCEPTIBILITY^a OF $\text{Ni}_2(\text{ac})_3(\text{saltNR}_2)_2$ COMPLEXES IN SOLID STATE

Compound	Temperature $^{\circ}\text{C}$	$\chi_g \times 10^6$	$\chi_M \times 10^6$	μ_{eff} (BM)
$\text{Ni}_2(\text{ac})_3(\text{saltNMe}_2)_2$	27	13.6	4356	3.24
$\text{Ni}_2(\text{ac})_3(\text{saltNNEt}_2)_2$	22	12.7	4295	3.22
$\text{Ni}_2(\text{ac})_3(\text{saltNBu}_2)_2$	27	11.6	4271	3.21

^a χ_g and χ_M are gram and corrected molar susceptibilities respectively in the solid state per nickel atom.

TABLE III.3

MAGNETIC SUSCEPTIBILITY^a DATA FOR $\text{Ni}_2(\text{ac})_3(\text{saltnNR}_2)$ COMPLEXES IN CHLOROFORM

Compound	Temperature °C	$\chi_g \times 10^6$	$\chi_M \times 10^6$	μ_{eff} (BM)
$\text{Ni}_2(\text{ac})_3(\text{saltnNMe}_2)$	20	13.75	4402	3.21
$\text{Ni}_2(\text{ac})_3(\text{saltnNNEt}_2)$	22	12.76	4295	3.20
$\text{Ni}_2(\text{ac})_3(\text{saltnNBu}_2)$	20	12.73	4510	3.26

^a χ_g and χ_M are gram and corrected molar susceptibilities respectively per nickel atom.

TABLE III.4

ABSORPTION MAXIMA (λ , nm) AND EXTINCTION COEFFICIENTS^a (ϵ , L.MOL⁻¹CM⁻¹) OF ELECTRONIC BANDS OF Ni₂(ac)₃(saltnNR₂) COMPLEXES IN BENZENE

Compound	$\lambda(\epsilon)$
Ni ₂ (ac) ₃ (saltnNMe ₂)	1,170(9) 635(11)
Ni ₂ (ac) ₃ (saltnNEt ₂)	1,170(10), 635(14)
Ni ₂ (ac) ₃ (saltnNBu ₂)	1,170(10), 650(13)

^a Solute concentrations were adjusted ($4-5 \times 10^{-3}$ M) so as to get the optical density value in the range 0.5-1.0. Extinction coefficients are per nickel atom.

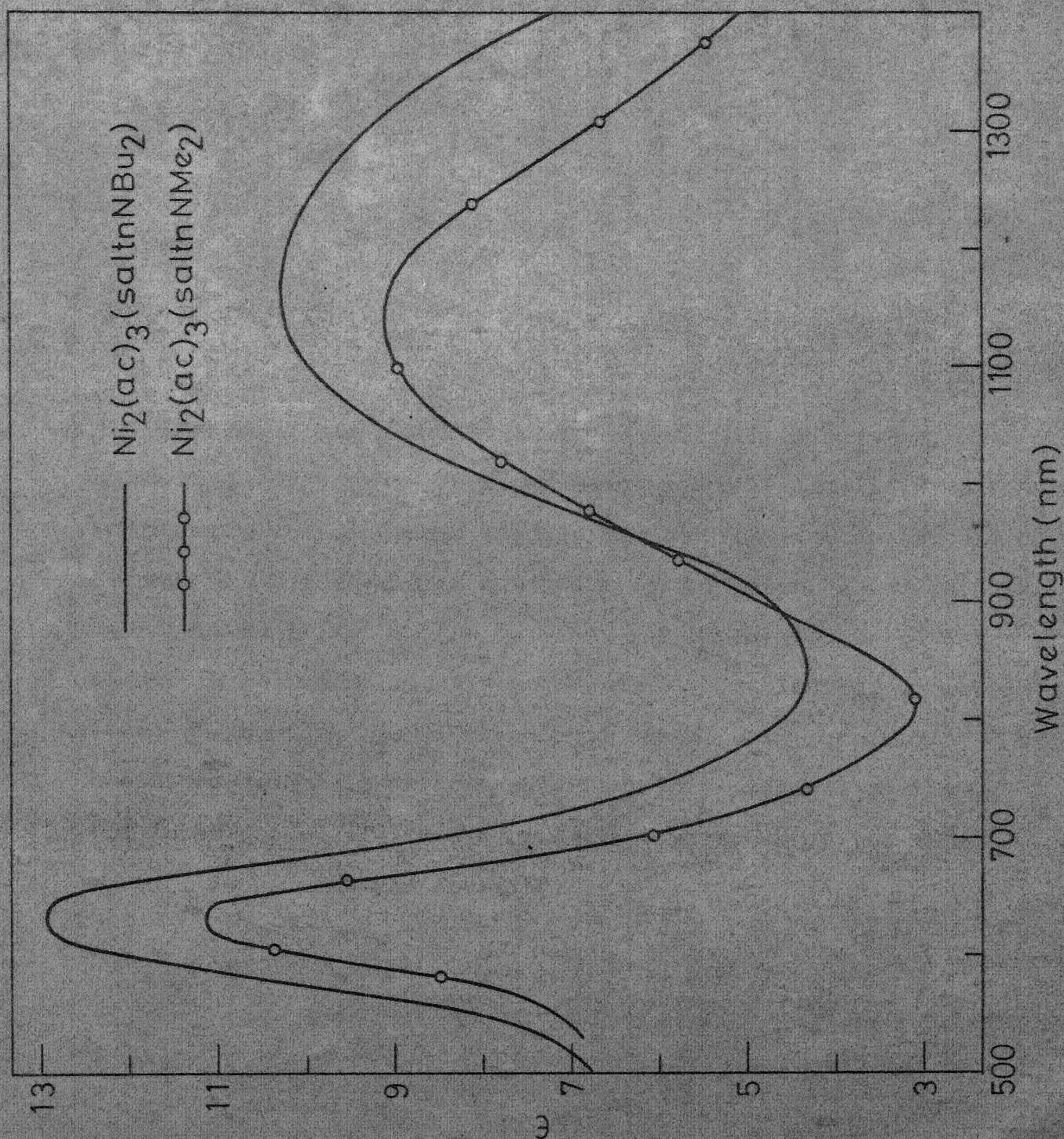
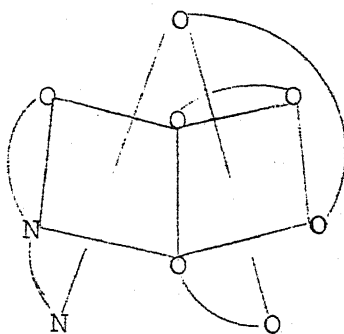


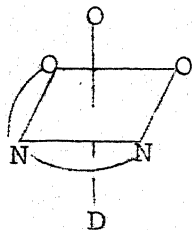
FIG. III.2 ELECTRONIC SPECTRA IN BENZENE

that species of the type $\text{Ni}_2(\text{ac})_3(\text{tridentate})$ with octahedral nickel(II) should exist. The $\text{Ni}_2(\text{ac})_3(\text{saltnNR}_2)$ system provides an example:



(II)

We have noted earlier that the reaction of $\text{Ni}_3(\text{ac})_6$ with salenNR_2 yields mononuclear pentacoordinated $\text{Ni}(\text{ac})(\text{salenNR}_2)$.³ No evidence for dinuclear species has been obtained with this ligand. The difference in the behaviour of salenNR_2 and saltnNR_2 can be rationalised on the basis of structure II. In this structure saltnNR_2 occupies three facial positions of an octahedron. The flexible $-(\text{CH}_2)_3-$ chain makes this possible.⁴ On the other hand salenNR_2 can only span in meridional positions⁵ (as in structure III) due to relative shortness of the $-(\text{CH}_2)_2-$ chain. It cannot span facially.



(III)

III.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Starting Chemicals

Salicylaldehyde was obtained from Bush and Co., London.

The N,N-dialkylpropylenediamines were obtained from Aldrich Chemical Co., U.S.A.

Acetylacetone was obtained from British Drug House, England.

b. Preparation of Complexes

i. Synthesis of bis(acetylacetonato)nickel(II)

A solution of acetylacetone (0.25 mol) in 50 ml methanol was added while stirring to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.125 mol) in water. To the resulting mixture was added a solution of 0.25 mol of sodium acetate in 75 ml water. The mixture was heated briefly on a hot plate. After allowing it to attain the room temperature, it was further cooled in the refrigerator for 6-8 hr. The blue green crystals of bis(acetylacetonato)-nickel(II) dihydrate⁶ were filtered off on a buchner funnel, washed with water and methanol. The dihydrate thus obtained was dried at 80° (5 mm) for 7-8 hr to yield deep green anhydrous⁷ compound.

ii. SaltnNR₂

The Schiff base was prepared by heating to reflux (0.5 hr) salicylaldehyde and the amine in equimolar proportions in ethanol. The solvent was removed on a rotary evaporator. The resulting brown liquid was used without further purification.

iii. Ni₂(ac)₃(saltnNR₂)

The Schiff base (0.1 mol) and Ni₃(ac)₆ (0.07 mol) were taken in 75 ml toluene. The reaction mixture was heated to reflux for 1 hr. The green solution was then filtered and cooled. Hexane was added to initiate crystallisation where needed. The green complex was obtained in 50% yield.

B. Characterization of Complexes

This was done by C, H, N, microanalysis and metal analysis. Characterization data for all complexes are collected in Table III.5.

The procedure for nickel analysis was the same as that described in Chapter II.

C. Solvents

Details are given in Chapter II.

D. Physical Measurements

a. Infrared Spectra

Details are given in Chapter II.

TABLE III.5

CHARACTERIZATION DATA FOR $\text{Ni}_2(\text{ac})_3(\text{saltnNR}_2)$ COMPLEXES

Compound	Mp °C ^a	% C		% H		% N		% Ni ^b	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{Ni}_2(\text{ac})_3(\text{saltnNMe}_2)$	201	52.30	52.28	6.08	6.08	4.52	4.17	18.93	18.97
$\text{Ni}_2(\text{ac})_3(\text{saltnNEt}_2)$	151	53.75	54.25	6.53	6.50	4.32	4.41	18.12	18.31
$\text{Ni}_2(\text{ac})_3(\text{saltnNBu}_2)$	160	56.28	56.30	7.15	6.96	3.97	4.06	16.67	16.58

^a All melting points are uncorrected.^b Nickel was estimated as dimethylglyoximate.

b. Electronic Spectra

Details are given in Chapter II.

c. Molecular Weight

Details are given in Chapter II.

d. Bulk Susceptibility Measurements

(i) Details of measurements on solid samples are given in Chapter II.

(ii) Solution measurements were made using split sample tubes. Distilled oxygen free water was used as a standard. The gram susceptibility of chloroform was found to be -0.05×10^{-6} at 25°C.

The densities of solutions were determined with a suitably designed specific gravity bottle.

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CHAPTER IV

STRUCTURE OF NICKEL(II) AND IRON(II) COMPLEXES OF 2-PHENYLAZOPYRIDINE*

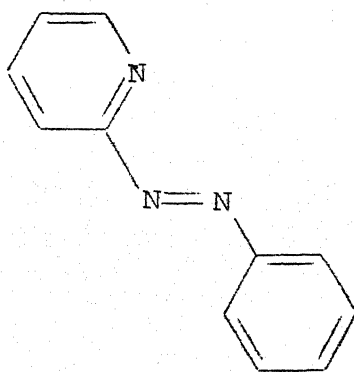
Abstract: 2-Phenylazopyridine (pap) acts as an unsymmetrical bidentate chelating ligand. The tris species $\text{Ni}(\text{pap})_3^{2+}$ and $\text{Fe}(\text{pap})_3^{2+}$ are isolated in the form of perchlorate and iodide respectively. The complex cations have pseudooctahedral geometry. From the ligand field spectrum of paramagnetic $\text{Ni}(\text{pap})_3^{2+}$, Dq of pap is calculated to be 1080 cm^{-1} , a value which is close to that of ethylenediamine in $\text{Ni}(\text{en})_3^{2+}$ but is considerably less

*The work described in this chapter has appeared in Ind. J. Chem., 14A, 166 (1976).

than that of chelating diimines, such as pyridinalimine. The isoelectric relationship between the diimine and azoimine fragments is noted. $\text{Fe}(\text{pap})_3^{2+}$ shows an intense band in the visible region which is assigned to charge transfer from metal t_{2g} (idealised O_h) to ligand π^* orbital. That the charge transfer state has contribution to the ground state is also evident from ir data. The N=N stretch is considerably lowered in $\text{Fe}(\text{pap})_3^{2+}$ in comparison to those in the ligand and in Ni(II) complexes. The paramagnetic mixed complexes $\text{Ni}(\text{pap})_2\text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ (X = Cl, Br) and diamagnetic $\text{Ni}(\text{pap})_2\text{I}_2$ are reported. On the basis of magnetic, electrical conductivity and electronic spectral data, it is suggested that $\text{Ni}(\text{pap})_2\text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ has pseudooctahedral Ni(II) with dichloromethane held in the crystal lattice but not influencing the Ni(II) environment in any major manner. In $\text{Ni}(\text{pap})_2\text{I}_2$ the two ligands are believed to be held in a planar manner.

IV.1 INTRODUCTION

In this and the next chapter, we present our work on metal (Ni, Fe) complexes obtained from ligands containing an azo group. An azo group suitably linked to an aromatic ring carrying additional donor sites is well suited for closure of a chelate ring. Good examples of such a situation are provided by the metal complexes of arylazophenols whose chelating activity has been known for many years.¹⁻³ A phenyl azo group attached to the 2-position of a pyridine ring as in 2-phenylazopyridine (I) may be expected to give stable metal chelates. This problem is explored for the first time in this chapter. Some related studies recently reported in literature are those on more complex systems such as 2,2'-, 3,3'- and 4,4'-azopyridines.⁴⁻⁶ The coordination chemistry of these ligands is often complicated by the formation of ligand and/or anion bridging.

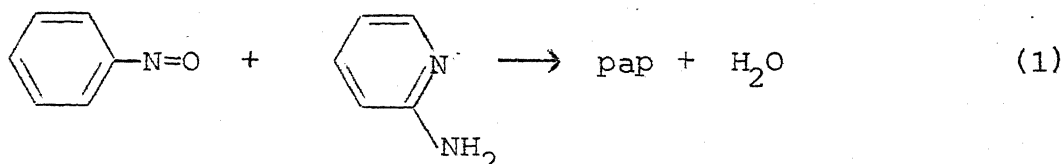


(I)

IV.2 RESULTS AND DISCUSSION

A. General Consideration

The ligand (I) which will be abbreviated as pap, is obtained in relatively poor yield by the reaction:⁷



The ligand readily reacts with Ni(II) salts yielding complexes of the type $\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$, $\text{Ni}(\text{pap})_2\text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ ($\text{X} = \text{Cl}, \text{Br}$) and $\text{Ni}(\text{pap})_2\text{I}_2$. In the crystalline state $\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$ is green while the other species are dark coloured. In dichloromethane or chloroform solution the respective colours are: $\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$, green; $\text{Ni}(\text{pap})_2\text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$, brownish green and $\text{Ni}(\text{pap})_2\text{I}_2$, brown. The dark coloured crystals of $\text{Fe}(\text{pap})_3\text{I}_2$ obtained by direct reaction between ferrous sulphate heptahydrate and the ligand (followed by the addition of potassium iodide) readily dissolve in water to yield deep blue solutions which are not very stable.

B. Tris Complexes

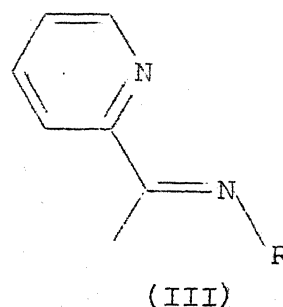
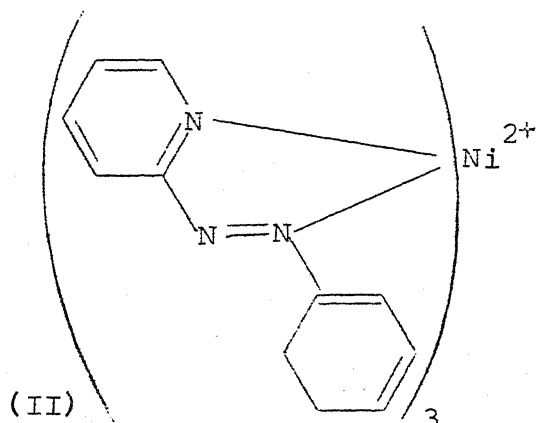
Electrical conductivity data are set out in Table IV.1. The observed values for $\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$ and $\text{Fe}(\text{pap})_3\text{I}_2$ falls within the range⁸ (150-160) expected for 1:2 electrolyte. Clearly the complex cation $\text{M}(\text{pap})_3^{2+}$ is present in these species.

TABLE IV.1

ELECTRICAL CONDUCTIVITY DATA IN NITROMETHANE

Compound	Temperature °C	Concentration mol.lit ⁻¹	Λ ohm ⁻¹ cm ² mol ⁻¹
Ni(pap) ₃ (ClO ₄) ₂	24	1.36 x 10 ⁻³ M	175
Fe(pap) ₃ I ₂	19	1.86 x 10 ⁻³ M	141
Ni(pap) ₂ Cl ₂ ·0.5CH ₂ Cl ₂	19	1.19 x 10 ⁻³ M	9
Ni(pap) ₂ Br ₂ ·0.5CH ₂ Cl ₂	19	1.31 x 10 ⁻³ M	16
Ni(pap) ₂ I ₂	19	0.93 x 10 ⁻³ M	45

$\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$ is fully paramagnetic (Table IV.2). In the electronic spectrum three bands are observed in the visible region (Fig. IV.1; Table IV.3). These bands can be readily assigned on the basis of a gross octahedral geometry (coordinative positions as shown in II) for the cation $\text{Ni}(\text{pap})_3^{2+}$. The



assignment is ${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})$, 920 nm; $\rightarrow {}^1E(\text{D})$, 855 nm and $\rightarrow {}^3T_{1g}(\text{F})$, 610 nm. The ${}^3A_2 \rightarrow {}^3T_{1g}(\text{P})$ transition is hidden under intense absorption in the uv. Since the energy of the ${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})$ transition is equal to $10 Dq$, the Dq value of pap, is calculated to be 1080 cm^{-1} . Interestingly this Dq value is considerably lower than that of 2-pyridinalimine (III) ($Dq = 1250 \text{ cm}^{-1}$) which is isoelectronic with pap. Evidently the azomethine is a stronger donor than the azo nitrogen. Infact the $10 Dq$ value of $\text{Ni}(\text{pap})_3^{2+}$ is close to that of $\text{Ni}(\text{ethylenediamine})_3^{2+}$.

$\text{Fe}(\text{pap})_3\text{I}_2$ is diamagnetic at room temperature. The metal atom thus has a low-spin d^6 configuration. The most characteristic feature of the electronic spectrum of $\text{Fe}(\text{pap})_3\text{I}_2$ (Fig. IV.2;

TABLE IV.2

MAGNETIC SUSCEPTIBILITY DATA

Compound	Temp. °C	$\chi_g \times 10^6$ ^a	$\chi_M \times 10^6$	μ_{eff} (BM)
Fe(pap) ₃ I ₂	22	Diamagnetic	-	-
Ni(pap) ₃ (ClO ₄) ₂	27.5	4.46	4014	3.12
Ni(pap) ₂ Cl ₂ ·0.5CH ₂ Cl ₂	22	6.74	3963	3.05
Ni(pap) ₂ Br ₂ ·0.5CH ₂ Cl ₂	22	5.92	4090	3.10
Ni(pap) ₂ I ₂	22	Diamagnetic	-	-

^a χ_g and χ_M are corrected gram and molar susceptibilities.

TABLE IV.3^{a,b}

ABSORPTION MAXIMA (λ , nm) AND EXTINCTION COEFFICIENTS
(ϵ , L. MOL⁻¹.CM⁻¹) OF SOME ELECTRONIC BANDS

Compound	Medium	λ (ϵ)
Fe(pap) ₃ I ₂	Water	590(5150); 550(3850) sh; 380(16900) sh; 320(37800).
Ni(pap) ₃ (ClO ₄) ₂	Solution (dichloro- methane)	920(12); 855(15) sh; 610(355); 325(38130)
Ni(pap) ₂ Cl ₂ .0.5CH ₂ Cl ₂	Solution (chloro- form)	1150(13); 605(122) sh; 445(510); 320(2390).
	Solid	1060; 610 sh; 430.
Ni(pap) ₂ Br ₂ .0.5CH ₂ Cl ₂	Solution (chloro- form)	1150(16); 590(202) sh; 440(1240) sh; 340(2825).
	Solid	1070; 615 sh; 410 sh.

^a sh = Shoulder.

^b The ligand pap shows bands at 445 and 340 nm.

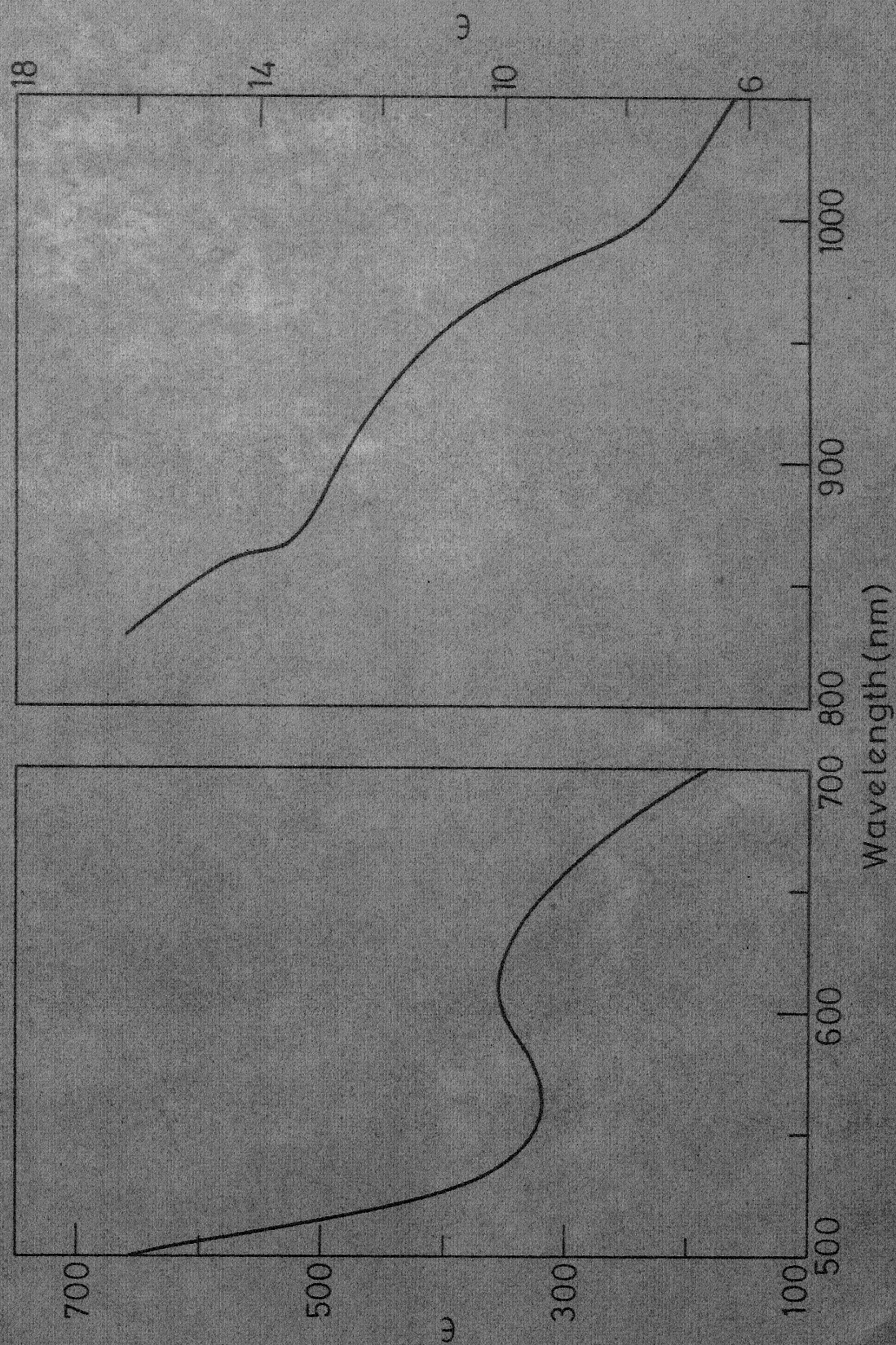


FIG. IV.1 ELECTRONIC SPECTRUM OF $\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$ IN DICHLOROMETHANE

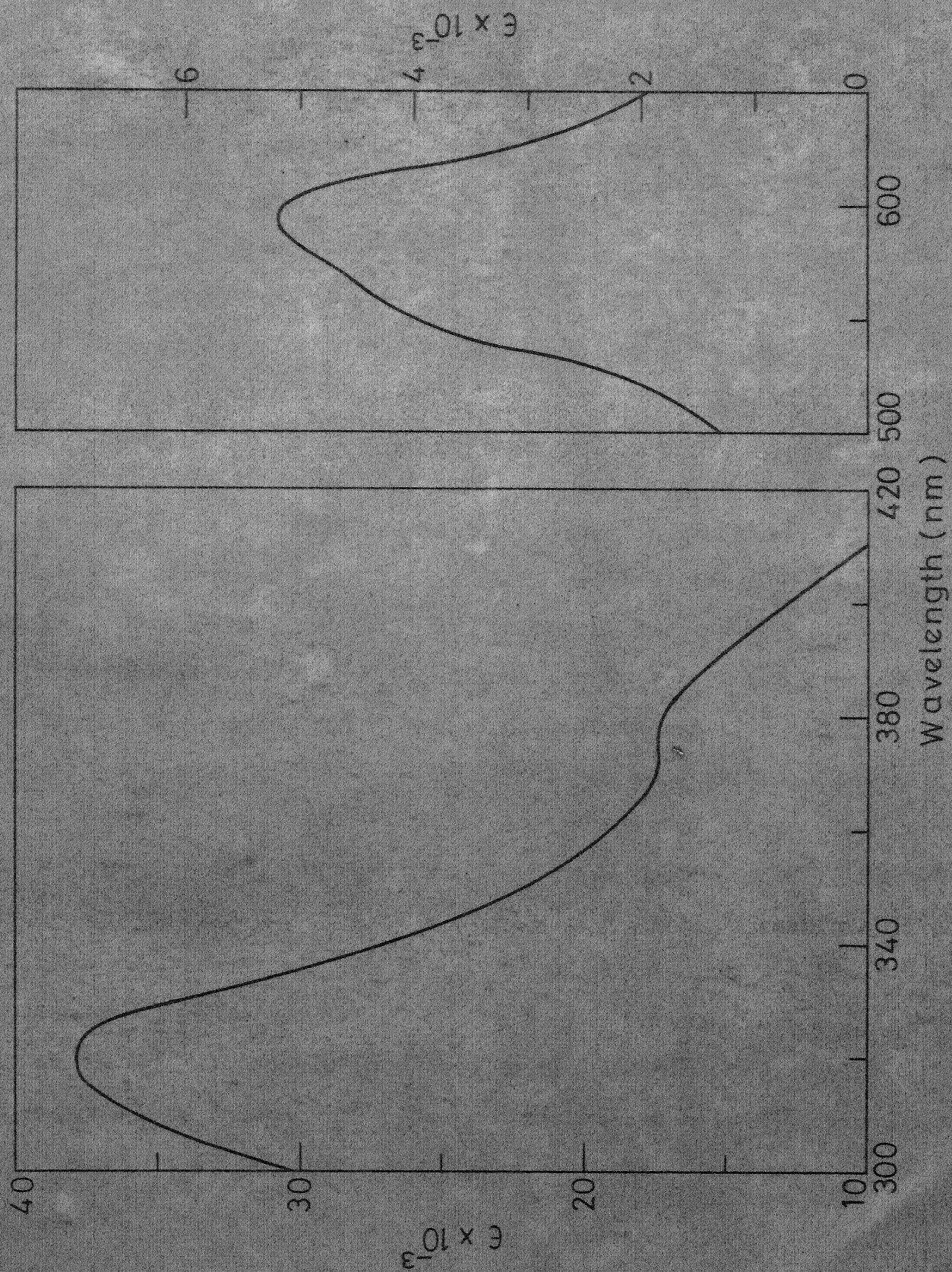
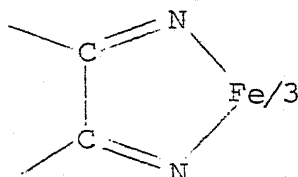


FIG. IV.2 ELECTRONIC SPECTRUM OF $\text{Fe}(\text{pap})_3\text{I}_2$ IN WATER

Table IV.3) is an intense band in the visible region near ~ 590 nm; there is a shoulder at slightly higher energy (550 nm). It is well known that tris diimine complexes of iron(II) (structural type IV), show an allowed charge transfer transition from metal



(IV)

t_{2g} orbital (idealised O_h) to lowest antibonding empty diimine π^* orbital.⁹⁻¹² This transition is seen in the form of a band at ~ 555 nm associated with a shoulder at slightly lower energies. The shoulder is believed to be the first member in a vibrational progression (coupling with $C=C + C=N$ vibrations). The azoimine group $-N=N-C=N-$ as present in pap is isoelectronic with the diimine function $-N=C-C=N-$. Consequently low energy metal-to-ligand charge-transfer transition may be expected in $Fe(pap)_3^{2+}$ also. Indeed the 590 nm band in the latter complex is undoubtedly due to such a transition. We note that the metal-to-ligand transition in $Fe(pap)_3^{2+}$ is at considerably lower energy than that in $Fe(diimine)_3^{2+}$. The higher Dq value (vide supra) of diimine ligand (IV) compared to the azoimine pap, may be partly responsible for this. $Fe(pap)_3^{2+}$ also shows a band at 380 nm. The origin of this band is not certain; the ligand itself has

absorption in this region (Table IV.3).

The infrared spectra of nickel(II) and iron(II) complexes were examined. Selected results are set out in Table IV.4. Our present concern is in the -N=N- stretching frequency. This frequency^{4,13} in the ligand and in Ni(pap)_3^{2+} and in other nickel(II) complexes described later fall in the narrow range $1418\text{--}1431\text{ cm}^{-1}$. On the other hand there is a dramatic decrease in this frequency to 1353 cm^{-1} in Fe(pap)_3^{2+} (Fig. IV.3). This is evidently due to some contribution of the metal-to-ligand charge transfer state(as discussed earlier) to the ground level as in the case of $\text{Fe(diimine)}_3^{2+}$ species.⁹⁻¹² The C=N stretching frequency $\sim 1600\text{ cm}^{-1}$ in Fe(pap)_3^{2+} is also lower than in the nickel(II) species. But the effect is not as pronounced as for the azo stretch. The ligand orbital involved in charge transfer evidently has a large proportion of azo character.

C. Structure of $\text{Ni(pap)}_2\text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ (X = Cl, Br)

These two compounds are fully paramagnetic (Table IV.2) in the solid state. The molar electrical conductivities of 1:1 electrolytes in nitromethane lie⁸ in the range $75\text{--}95\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. The observed conductivities of the present complexes show that they are only slightly dissociated in solution (Table IV.1). The dichloromethane of crystallisation is strongly held in the lattice and is not removed even at low pressure (5 mm) and elevated temperature (80°). Quite a few transition metal complexes which

TABLE IV.4^{a,b}SELECTED INFRARED FREQUENCIES (CM⁻¹)

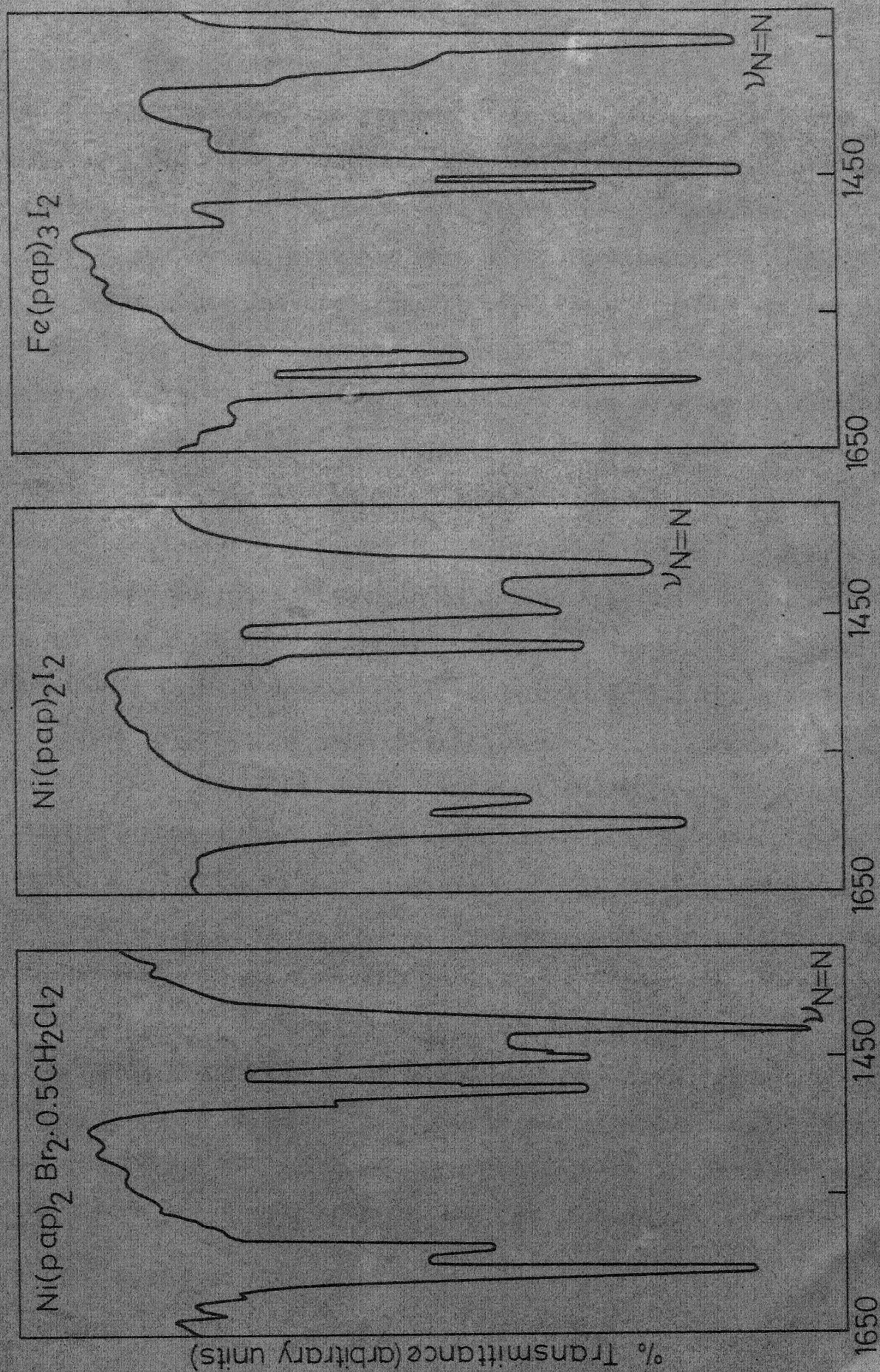
Assignment	pap	Fe(pap) ₃ I ₂	Ni(pap) ₃ (ClO ₄) ₂ ^c	Ni(pap) ₂ Cl ₂ , ^d O.5CH ₂ Cl ₂	Ni(pap) ₂ Br ₂ , ^d O.5CH ₂ Cl ₂	Ni(pap) ₂ I ₂
Aromatic	1616(s)	1599(s)	1605(s)	1605(s)	1604(s)	1600(s)
C=C & C=N	1587(m)	1579(m)	1586(m)	1586(m)	1587(m)	1582(m)
	1477(m)	1458(m)	1484(m)	1472(m)	1468(m)	1468(m)
	1456(s)	1446(s)	1446(s)	1452(m)	1446(s)	1447(s)
N=N	1425(s)	1353(s)	1428(s)	1431(s)	1426(s)	1418(s)
C-H out-of-plane bending in phenyl ring	687(s)	692(s)	691(s)	698(s)	692(s)	692(s)
C-H out-of-plane bending in pyridine ring	784(s)	772(s)	770(s)	773(s)	765(s)	770(s)

a. An unassigned band of medium intensity appears in the range 740-750 cm⁻¹ in all compounds studied. All spectra are run in KBr discs.

b. Symbols in parentheses refer to relative intensity; s, strong; m, medium.

c. ν_3 of ClO₄ is observed as a broad band of high intensity centred at 1100 cm⁻¹.

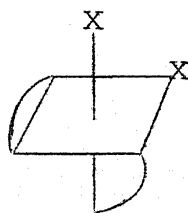
d. C-Cl stretch of CH₂Cl₂ is at 726 cm⁻¹(m).

FIG.IV.3 SELECTED INFRARED FREQUENCIES (cm^{-1})

contain dichloromethane of crystallisation are known.¹⁴ We wish to stress that the present compounds can also be prepared as amorphous powders without the dichloromethane of crystallisation. On the other hand, well-formed crystals which are easy to purify are obtained when dichloromethane is present. The solid state infrared spectra of $\text{Ni}(\text{pap})_2\text{Br}_2$ and $\text{Ni}(\text{pap})_2\text{Br}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ were found to be essentially superimposable except that the latter compound shows bands characteristic of dichloromethane also. The dichloromethane of crystallisation does not appear to affect the ligand disposition in any major way.

Considerable interest has been shown in recent years about the stereochemistry of complexes of the type $\text{Ni}(\text{Lb})_2\text{X}_2$ where Lb is a bidentate ligand. There is evidence¹⁵ that when X is widely separated from Lb in the spectrochemical series, the cis configuration is preferred over the trans structure. Good examples are $\text{Ni}(\text{phen})_2\text{X}_2$,¹⁵ $\text{Ni}(\text{en})_2\text{X}_2$ ¹⁶ (dimer) and $\text{Ni}(\text{po})\text{X}_2$ ¹⁷ where phen = o-phenanthroline, en = ethylenediamine, po = 2-pyridinal-oxime and X = Cl, Br, I. In going from NiN_6 to trans- NiN_4X_2 , the octahedral ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_1)$ band shows observable splitting due to decrease of symmetry from O_h to D_{4h} . A good example is trans- $\text{Ni}(\text{py})_4\text{Br}_2$.^{17,18} The cis- NiN_4X_2 sphere has a lower symmetry (C_{2v}) than trans- NiN_4X_2 but the magnitude of orbital splitting is expected to be less.¹⁹ In practice such splitting is often not observed.^{15,17} The complexes of 2-phenylazopyridine under discussion shows an unsplit ν_1 band at 1070 nm (solid) or at

1150 nm (solution) (Fig. IV.4). Previously we have noted that 2-phenylazopyridine and ethylenediamine have similar ligand field strengths. In this context it is significant that ν_1 of solid $\text{Ni(en)}_2\text{Cl}_2$ (dimer) is at 980 nm,¹⁷ a value which is very close to that of the presently synthesised $\text{Ni(pap)}_2\text{Cl}_2$. However, $\text{Ni(pap)}_2\text{Cl}_2$ unlike the ethylenediamine complex cannot be dimeric, in view of the electrical conductivity data (vide supra). On the basis of above discussion we propose that $\text{Ni(pap)}_2\text{X}_2$ has structure V. Far infrared studies could throw important light on this problem. Unfortunately, we do not have facilities for obtaining ir spectra below 250 cm^{-1} .



(V)

D. $\text{Ni(pap)}_2\text{I}_2$

This is diamagnetic and shows no ligand field bands below 700 nm. In this complex the Ni(pap)_2 sphere is grossly planar presumably with a trans (steric over crowding of phenyl groups in cis geometry) disposition of ligand molecules (VI). The iodide ions seem to remain partially bound (weak axial coordination) in solution, since the observed electrical conductivity

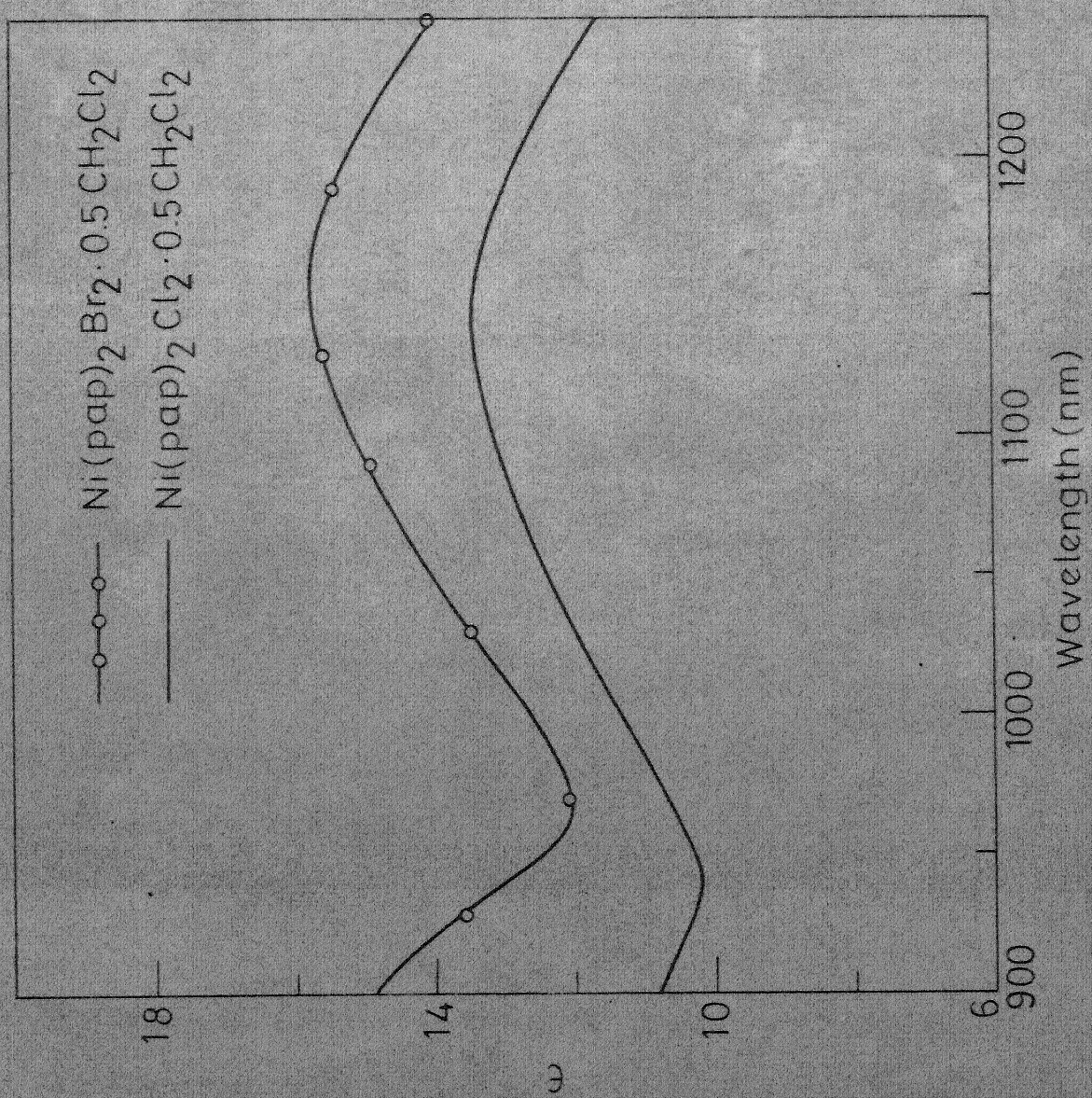
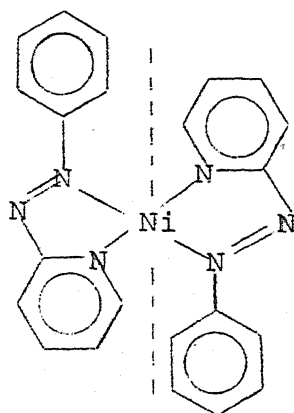


FIG. IV. 4 ELECTRONIC SPECTRA OF $\text{Ni(pap)}_2 \text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$
IN CHLOROFORM

is much lower than that expected for a 1:2 electrolyte. In view of the proposed difference in stereochemistry of $\text{Ni}(\text{pap})_2$ fragment in the chloro (or bromo) and iodo complexes, it may be significant that the $-\text{N}=\text{N}-$ stretch in former (no centre of symmetry) is more intense than that of the latter (centre of symmetry).



(VI)

IV.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Starting Chemicals

- i. Nitrosobenzene was synthesised as described in the literature.²⁰
- ii. 2-Aminopyridine was obtained by British Drug House, England.
- iii. Preparation of 2-phenylazopyridine:⁷ 5.1 g of 2-aminopyridine was added to a warm 50% NaOH solution (50 ml). The mixture was gently heated after adding a little benzene (3 ml). 6 g of

nitrosobenzene was added slowly. The entire mixture was extracted several times with benzene. The dark brown solution was boiled with charcoal and filtered. The filtrate was concentrated under reduced pressure to 25 ml. The concentrate was subjected to column chromatography, eluting it with benzene. The lower most layer (green and dirty brown) was discarded. The orange band was collected. The evaporation yielded reddish needles of 2-phenylazopyridine. It should be noted that the yield of this preparation was very poor (30%). Often the orange liquid did not solidify, which was used as such for the preparation of complexes.

b. Preparation of Complexes

i. $\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$

A solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.001 mol) in methanol was added to a solution of pap (0.003 mol) in the same solvent. The colour of the reaction mixture turned dark-green. The mixture was kept overnight at room temperature. The dark green crystals formed were filtered, washed with little methanol and dried (5 mm, 80°C). The yield was 50%.

ii. $\text{Fe}(\text{pap})_3\text{I}_2$

An aqueous ethanolic solution containing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.001 mol) and pap (0.003 mol) was warmed and to this concentrated potassium iodide solution was added. On cooling to 5°C , violet crystals were deposited. These were recrystallised from water

containing dissolved potassium iodide. The yield was 60%.

iii. $\text{Ni}(\text{pap})_2\text{Cl}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$

A methanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.001 mol) was added to a methanolic solution of the ligand (0.002 mol). The solvent was removed by heating on a steam-bath. The resulting gum was extracted with dichloromethane. The extract was concentrated and cooled to room temperature. A dark coloured crystalline solid deposited which was then recrystallised from dichloromethane. The crystals analysed as $\text{Ni}(\text{pap})_2\text{Cl}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$, yield was 50%.

iv. $\text{Ni}(\text{pap})_2\text{Br}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$

The bromo compound was prepared using the above procedure starting from NiBr_2 .

v. $\text{Ni}(\text{pap})_2\text{X}_2$ (X = Cl, Br)

When chloroform was used as the solvent for extracting the gum in the above preparations dark-green amorphous powder of composition $\text{Ni}(\text{pap})_2\text{X}_2$ were obtained. The chloroform does not enter the lattice, unlike dichloromethane.

vi. $\text{Ni}(\text{pap})_2\text{I}_2$

A methanolic solution containing $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.001 mol) and ligand (0.002 mol) was gently warmed. Potassium iodide

solution was then added to this mixture. The dark solid thus obtained yielded dark crystals (brown when powdered) on recrystallisation from chloroform-hexane mixture. Yield was 60%.

B. Characterization of Complexes

This was done by C, H, N microanalysis and metal analysis. Characterization data for all complexes are collected in Table IV.5.

The procedure for nickel analysis was the same as described in Chapter II.

Iron Estimation

100 mg of sample was taken in a conical flask and 5 ml of conc. HNO_3 was added. The mixture was heated to boil. Brown fumes started evolving. When the brown fumes subsided, 10 ml of HCl was introduced and the mixture was again heated to boil. A clear pale yellow solution was obtained. The heating was continued to evaporate almost all the acid. 25 ml of water was added. An aqueous ammonia solution was then added dropwise, till a faint brownish precipitate persisted, which was dissolved by adding minimum quantity of 1N HCl. Then 1.5 g of ammonium acetate in 70 ml water was added followed by oxine solution (2 per cent in N-acetic acid) from a burette with constant stirring until a slight excess was present. About 6-7 ml was required. The dark precipitate thus obtained was digested on a water bath for 1 hr,

TABLE IV.5

CHARACTERIZATION DATA

Compound	%C		%H		%N		% Metal	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$\text{Fe}(\text{pap})_3\text{I}_2$	46.10	46.35	3.14	3.43	14.66	14.79	6.50	6.45
$\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$	49.00	49.28	3.37	3.52	15.60	15.80	7.27	7.10
$\text{Ni}(\text{pap})_2\text{Cl}_2 \cdot 0.5\text{CH}_2\text{Cl}_2^{\text{a}}$	48.70	48.43	3.36	3.21	15.49	15.24	10.82	10.60
$\text{Ni}(\text{pap})_2\text{Br}_2 \cdot 0.5\text{CH}_2\text{Cl}_2^{\text{b}}$	42.47	42.26	2.89	3.02	13.04	13.15	9.11	9.23
$\text{Ni}(\text{pap})_2\text{I}_2$	38.88	38.43	2.65	2.86	12.37	12.43	8.65	8.84

a. The percentage of chloride directly bound to nickel, Calcd: 13.07; Found: 12.72.

b. The percentage of bromide directly bound to nickel, Calcd: 24.80; Found: 24.90.

filtered through a preweighed sintered crucible, washed successively with 1% acetic acid and water. It was dried in hot air oven at 125-135°C to constant weight. It was weighed as $\text{Fe}(\text{C}_6\text{H}_5\text{OH})_3$.

C. Solvents

Details are given in Chapter II.

D. Physical Measurements

a. Infrared Spectra

Details are given in Chapter II.

b. Electronic Spectra

Details are presented in Chapter II.

c. Bulk Susceptibility Measurements

Details of measurements of solid samples are available in Chapter II.

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CHAPTER V

MIXED METAL COMPLEXES OF ARYLAZOOXIMES

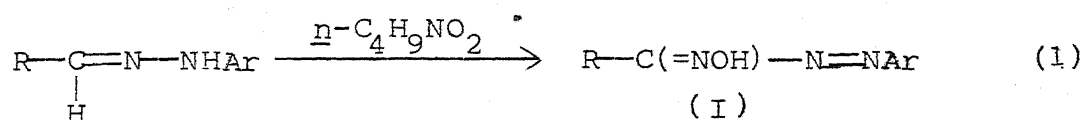
Abstract: Arylazooximes ($R-C(=NOH)-N=N-Ar$) abbreviated as HaaO, have the azoimine fragment which strongly binds iron(II) giving rise to five-membered chelate rings (ir data). The tris chelate $Fe(aao)_3^-$ is green in colour due to the presence of a strong metal \rightarrow ligand charge transfer transition at ~ 600 nm. This ion can be isolated in the form of the sodium salt $NaFe(aao)_3 \cdot H_2O$ in which, $Fe(aao)_3^-$ has cis geometry (pmr data). The sodium ion is believed to be bound to the water molecule and to oxime oxygen atoms. $NaFe(aao)_3 \cdot H_2O$ is poorly conducting in nitromethane solution. It is soluble in a variety of organic solvents including benzene. On reaction with acid it produces $HFe(aao)_3$ in

which the proton is believed to be chelated (intermolecularly or intramolecularly) to $\text{Fe}(\text{aao})_3^-$ via the oxime oxygen atoms. Reaction of HaaO with FeCl_3 produces a crystalline solid which has been shown to be an intervalence species of the type $[\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}}(\text{aao})_3)_2]\text{Fe}^{\text{III}}\text{Cl}_4$ (1:1 electrolyte in nitromethane and nitrobenzene). In this both iron(III) atoms are high-spin. The iron(III) atom in the cation is most probably bound in an octahedral fashion to the six oximate oxygen atoms of two cis- $\text{Fe}(\text{aao})_3^-$ moieties. The presence of Fe-O and Fe-Cl stretches has been identified in the infrared region. The corresponding perchlorate $[\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}}(\text{aao})_3)_2]\text{ClO}_4$ is obtained by a direct reaction between iron(II) perchlorate and HaaO. The chemical interconversion of the various species viz., $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$, $\text{HFe}(\text{aao})_3$, $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ and $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ are described. For example $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ reacts with sodium hydroxide to yield two moles of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ and two moles of iron(III) hydroxide. On the other hand $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ reacts with one mole of FeCl_3 to regenerate $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$. The species $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{Br}$ and $\text{Ni}[\text{Fe}(\text{aao})_3]_2$ are briefly described. The $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ ($\text{X} = \text{ClO}_4, \text{Br}$) shows a $g' \sim 4.3$ epr line characteristic of rhombic FeO_6 sphere. When $\text{X} = \text{FeCl}_4$, an intense additional band at $g \sim 2.0$ (due to FeCl_4^-) is also observed.

V.1 INTRODUCTION

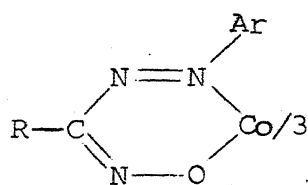
In this chapter mixed arylazooxime complexes of sodium(I), iron(II) and iron(III) are described.

The arylazooximes (I) are obtained^{1, 2} by nitrosation of arylhydrazones of aldehydes with n-butyl nitrite:

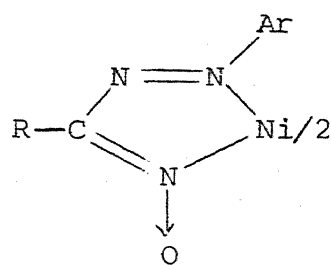


Previous work from this laboratory^{2, 3} has shown that the arylazooximes are extensively hydrogen bonded and exhibit cis-trans isomerism (around C=N) in solution. In what follows the ligand (I) will be abbreviated as HaaO and its conjugate base $[\text{R}-\text{C}(=\text{NO})-\text{N}=\text{NAr}]^-$ as aao.

Many years ago Fiegl⁴ studied the "salt formation" ability of phenylazoacetaldoxime with copper(II). Hunter and Roberts⁵ first observed that arylazooximes undergo a fast reaction with cobalt(II) acetate in alcohol producing purple tris complexes of trivalent cobalt $\text{Co}(\text{aao})_3$. They suggested without any substantial evidence a six membered chelate ring (II). Malatesta and Pizzoti⁶ described the diamagnetic bis complexes of nickel(II) which they formulated as (III) with five membered chelate rings. The infrared, electronic and pmr spectra of $\text{Co}(\text{aao})_3$ ⁷ and $\text{Rh}(\text{aao})_3$ ⁸ were studied in this laboratory some time ago. The chelate rings were concluded to be five-membered (IV). The

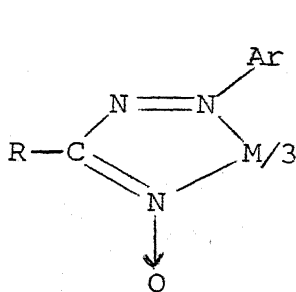


(II)

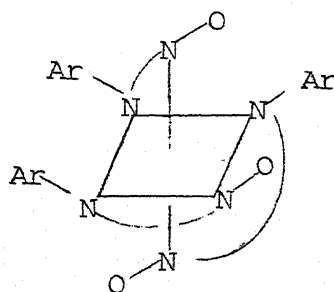


(III)

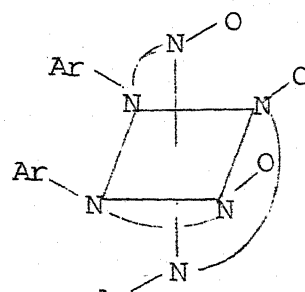
stereochemistry in the cobalt(III) complex is exclusively trans (V) while the rhodium(III) complexes exist in both cis (VI) and trans (V) forms. The observed stereochemistry is related^{7,8} to



(IV)

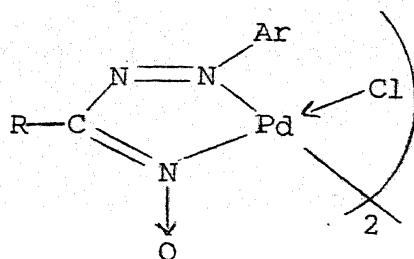


(V)



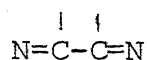
(VI)

ligand steric hindrance and metal ion size. Palladium(II) forms halogen bridged complexes (VII) and bis complexes (type III) with arylazooximes. These undergo many bridge splitting and/or chelate ring opening reactions.⁹ The dinuclear copper(II) species of the type $\text{Cu}_2(\text{aao})_4$ are strongly exchange coupled and are diamagnetic.¹⁰

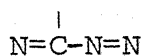


(VII)

In view of the fact that Haao gives rise to neutral tris complexes $M(aao)_3$ with cobalt(III) and rhodium(III), it was felt that it will be interesting to obtain the corresponding iron(III) complexes. On the other hand, it is known that ligands having α -diimine function (VIII) readily form^{11,12} deeply coloured-usually cationic-stable complexes of iron(II). Since the arylazooximes contain the α -azoimine group (IX) which is isoelectronic with VIII, it was thought that arylazooximes may form stable iron(II) complexes, having interesting spectroscopic and other properties (compare with 2-phenylazopyridine (Chapter IV) which also has the function IX).



(VIII)



(IX)

V.2 RESULTS AND DISCUSSION

A. Synthetic Experiments

In neutral or ammoniacal aqueous solution Haao does not undergo any observable reaction with iron(III) salts such as ferric ammonium sulphate. However, it readily reacts with anhydrous ferric chloride in 95% ethanol. On mixing the reagents, the reaction mixture develops an immediate dark colour. On gentle heating for a few minutes black crystalline solid of composition $Fe(aao)_{1.5}Cl$ deposits from the solution. This

compound alone could be isolated even when the Hao:FeCl_3 ratio is made 3:1. Best yields however were obtained when the ratios were 3:2.

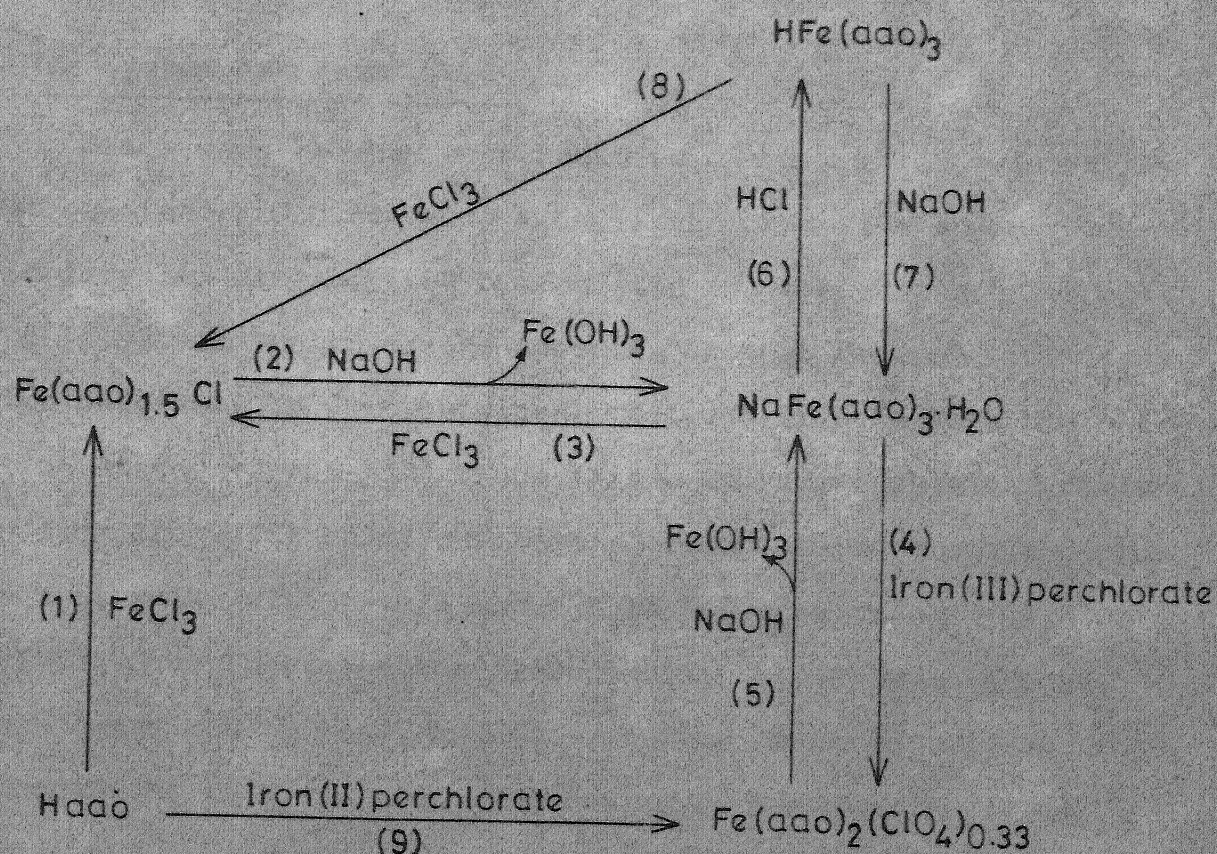
$\text{Fe(aao)}_{1.5}\text{Cl}$ is only sparingly soluble in ethanol, benzene and water. However, it readily dissolves in polar organic solvents such as chloroform, acetone, nitromethane, nitrobenzene etc. giving greenish black solutions. Reaction of an acetone solution with aqueous sodium hydroxide leads to the rejection of Fe(OH)_3 and the formation of a green solution. From this solution $\text{NaFe(aao)}_3\cdot\text{H}_2\text{O}$ can be readily isolated in the form of green crystals, which are more or less soluble without any change of colour in a variety of solvents such as benzene, acetone, ethanol, nitromethane, nitrobenzene, water etc. Reaction of $\text{NaFe(aao)}_3\cdot\text{H}_2\text{O}$ with anhydrous FeCl_3 in warm 95% ethanol regenerates $\text{Fe(aao)}_{1.5}\text{Cl}$.

When a solution of $\text{NaFe(aao)}_3\cdot\text{H}_2\text{O}$ in ethanol is treated with dilute HCl , a black crystalline precipitate of composition HFe(aao)_3 results. This can be reacted with sodium hydroxide to regenerate $\text{NaFe(aao)}_3\cdot\text{H}_2\text{O}$. The solubility characteristics of HFe(aao)_3 are similar to those of $\text{Fe(aao)}_{1.5}\text{Cl}$.

Lastly the reaction of iron(II) perchlorate hexahydrate with Hao, in warm 95% ethanol readily yield black crystals of composition $\text{Fe(aao)}_2(\text{ClO}_4)_{0.33}$. Its solubility characteristics are again similar to those of $\text{Fe(aao)}_{1.5}\text{Cl}$.

The reactions described above are summarised in Fig.

V.1. The species involved here are then: $\text{NaFe(aao)}_3\cdot\text{H}_2\text{O}$,



Solvents

(1), (3), (4), (7), (8), (9) : 95% Ethanol

(6) : Aqueous ethanol

(2), (5) : Acetone

FIG.V.1 CHEMICAL INTERCONVERSION OF ARYLAZOOXIMATES

HFe(aao)_3 , $\text{Fe(aao)}_{1.5}\text{Cl}$ and $\text{Fe(aao)}_2(\text{ClO}_4)_{0.33}$. These will now be taken up for discussion.

B. The System $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$

Since each aao has unit negative charge, it is evident that $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ contains iron in the oxidation state +2. This is fully corroborated by magnetic and spectral data reported in this section. It will be shown later that $\text{Fe(aao)}_{1.5}\text{Cl}$ (from which $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ is obtained) contains iron in both the oxidation states +2 and +3. Since this compound is obtained starting from iron(III) chloride, partial reduction must occur during the synthesis. It is well known that FeCl_3 is reduced by alcohol to FeCl_2 under photochemical irradiation.¹³ It appears that ethanol can reduce FeCl_3 thermally in the presence of HaaO. The mechanism of this reduction was not investigated.

a. Magnetic Data

The $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ system is diamagnetic. After diamagnetic correction, the iron atom is found to be slightly paramagnetic. Two representative examples are shown in Table V.1. The slight paramagnetism of the iron atom is undoubtedly due to temperature independent contributions to susceptibility. The absence of unpaired electrons in this system is corroborated by pmr data, which will be presented later. The low-spin (t_{2g}^6) nature of $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ will be in agreement with a structure,

TABLE V.1

MAGNETIC SUSCEPTIBILITY DATA FOR $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$

Ar=	Compound R=	Temp. °C	$\chi_g \times 10^6$ ^a	$\chi_M \times 10^6$	μ_{eff} (BM)
C_6H_5	C_6H_5	20.0	-0.39	37	0.29
C_6H_5	$\text{p-CH}_3\text{-C}_6\text{H}_4$	20.5	-0.38	33	0.28

a. χ_g and χ_M are gram and corrected molar susceptibilities.

TABLE V.2

INFRARED DATA OF SOME ARYLAZOOXIMES AND $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$
COMPLEXES IN KBr (DISCS)

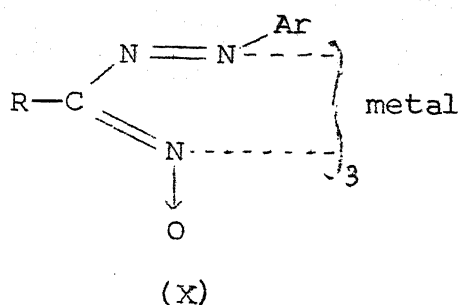
Free ligand R=Ar= C_6H_5	$\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ R=Ar= C_6H_5	Free ligand Ar= C_6H_5 R= $\text{p-CH}_3\text{-C}_6\text{H}_4$	$\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ Ar= C_6H_5 R= $\text{p-CH}_3\text{-C}_6\text{H}_4$	Assign- ment
3260	3400	3180	3360	$\nu_{\text{O-H}}$ ^a
1635	1605	1630	1595	$\nu_{\text{C=N}}$ ^b
1038	1280, 1242 ^d	1050	1280, 1250 ^d	$\nu_{\text{N-O}}$ ^c
690, 715, 770	690, 730, 760	690, 760, 770	700, 765	out-of- plane δ_{CH}

^a broad band; ^b weak band; ^c strong band; ^d either or both
could be $\nu_{\text{N-O}}$.

in which iron(II) has a pseudooctahedral FeN_6 coordination sphere. The implication is that the $\text{Fe}(\text{aao})_3^-$ unit may have a structure very similar to that of the isoelectronic $\text{Co}(\text{aao})_3$ species (structure V and VI). However, the iron(II) system has the complication in that binding to Na^+ is to be accounted for. This point will be discussed (vide infra).

b. Infrared Data

Vibration spectra of free arylazooximes in the solid state and in solution show an intense and some what broad band (width at half-height $\sim 50 \text{ cm}^{-1}$) in the region $1000\text{--}1050 \text{ cm}^{-1}$. This has been assigned² to $\nu_{\text{N-O}}$ of the azooxime moiety. A weak band at $\sim 1630 \text{ cm}^{-1}$ is due to the C=N stretch.² On complex formation (e.g., $\text{Co}(\text{aao})_3$) the N-O stretch is shifted^{7,8} very considerably to higher frequency due to the contribution of the nitron structure X.⁷ Similar shifts to high frequency occur in $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$.



In fact spectra of these complexes are very similar to those of $\text{Co}(\text{aao})_3$. Some selected frequency data are set-out in Table V.2. Unlike $\nu_{\text{N-O}}$, the C=N stretch is shifted to lower frequencies on complexation. This is expected. The N=N stretch should appear

at $\sim 1400 \text{ cm}^{-1}$ (compare Chapter IV). However, arylazooximes show a complex spectrum in this region and we have not been able to identify $\nu_{\text{N}=\text{N}}$ with certainty. At the present level of analysis, infrared data alone do not settle the structural question unequivocally. However, indications are strong that a $\text{Co}(\text{aao})_3^-$ like species (i.e., $\text{Fe}(\text{aao})_3^-$) is present.

c. Electronic Spectra

In the electronic spectra² of free arylazooximes, an $n-\pi^*$ azo band is clearly seen in the region 455-400 nm ($\epsilon < 1000 \text{ l.mol}^{-1} \text{ cm}^{-1}$). The next band is of $\pi-\pi^*$ origin and is located at $\sim 300 \text{ nm}$. The features in the spectrum of the potassium salt of Haao are found to be essentially similar to those of the parent oxime.

Since the complexes under discussion contain the azoimine fragment (IX), one may expect the presence of metal-ligand charge transfer transitions in the visible region as in the case of 2-phenylazopyridine-iron(II) system, $\text{Fe}(\text{pap})_3^{2+}$ (Chapter IV). Indeed an intense band at $\sim 600 \text{ nm}$ with an ill-defined shoulder at a slightly higher energy is present in the spectra of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ (Table V.3 and Fig. V.2). This band can be assigned to the $t_{2g} \rightarrow \pi^*$ (azoimine) transition as in the case of $\text{Fe}(\text{pap})_3^{2+}$. Interestingly the band positions of $\text{Fe}(\text{aao})_3^-$ and $\text{Fe}(\text{pap})_3^{2+}$ are nearly the same. The $\text{Fe}(\text{aao})_3^-$ system also shows a band at $\sim 400 \text{ nm}$. A similar band is observable in the Haao complexes of cobalt(III),⁷ copper(II)¹⁰ and palladium(II).¹⁴ This band may

TABLE V.3

ABSORPTION MAXIMA (λ , nm) AND EXTINCTION COEFFICIENTS (ϵ , L.MOL⁻¹.CM⁻¹)
OF NaFe(aao)₃.H₂O COMPLEXES IN CHLOROFORM SOLUTIONS

Compound		$\lambda(\epsilon)$
Ar =	R =	
C ₆ H ₅	CH ₃	610(9,200); 545(6,900) sh; 380(26,000)
C ₆ H ₅	n-C ₃ H ₇	610(9,500); 545(7,100) sh; 380(24,000)
C ₆ H ₅	C ₆ H ₅	610(9,720); 540(7,400) sh; 400(17,600)
C ₆ H ₅	p-CH ₃ -C ₆ H ₄	610(10,600); 540(7,500) sh; 405(15,800)

sh: Shoulder.

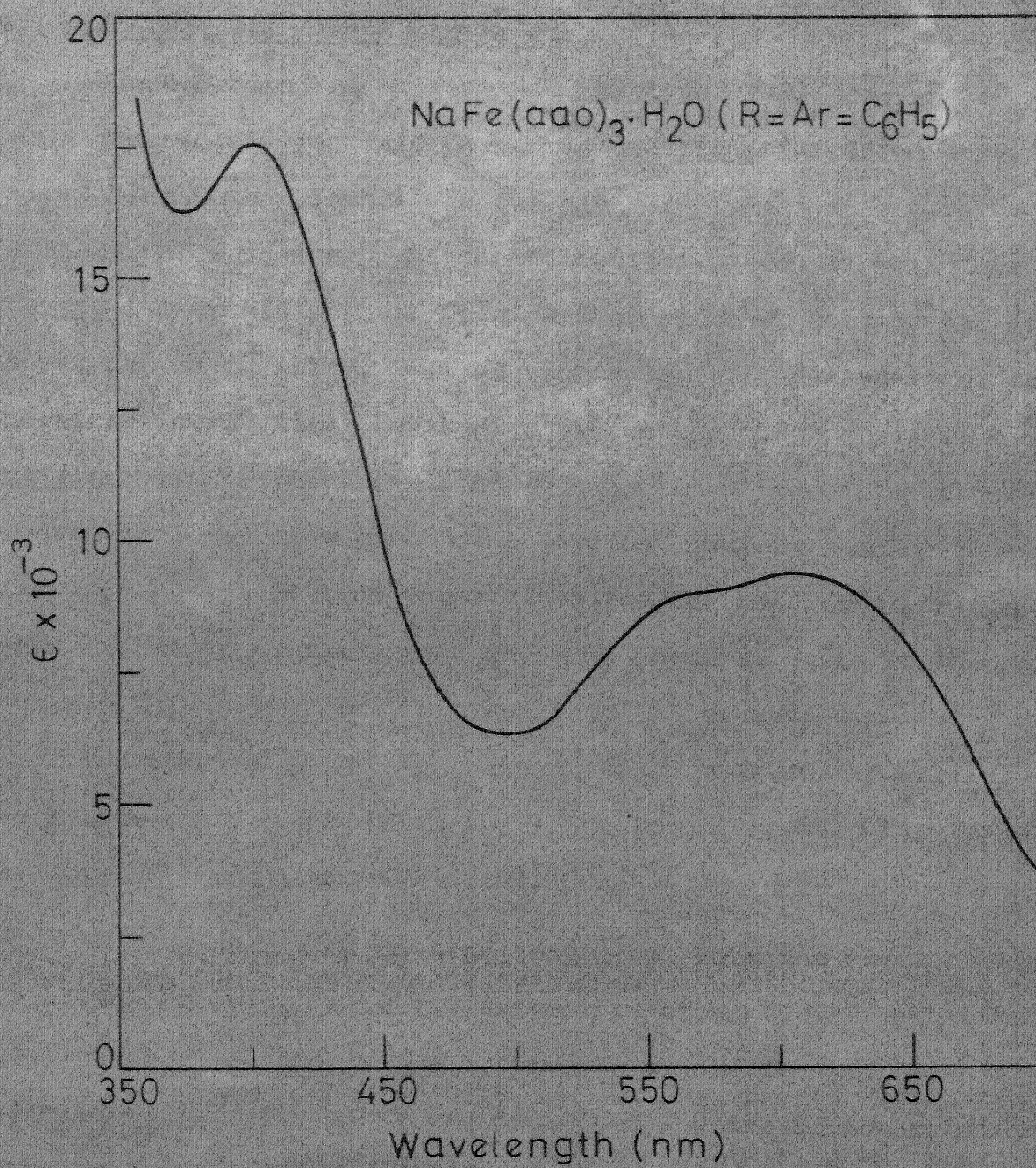


FIG. V.2 ELECTRONIC SPECTRUM IN CHLOROFORM

represent metal perturbed ligand transitions.

d. Proton Magnetic Resonance Spectra

Pseudooctahedral chelates of the type $M(AB)_3$ can exist in two geometrically isomeric forms cis and trans (AB is an unsymmetrical bidentate ligand). In the cis form, the A ends span facially while in the trans form the distribution is meridional. The cis isomer has a three-fold axis of symmetry whereas the trans isomer has no symmetry. In the cis isomer all chelate rings are therefore in identical environments. On the other hand, in the trans isomer all three chelate rings are in different environments. A given nucleus (or a group of equivalent nuclei) should, in principle have different chemical shifts for the three chelate rings in the trans isomer and the same chemical shift in the cis isomer. This principle¹⁵ has been used^{7,8} to establish the stereochemistries of $Co(aao)_3$ and $Rh(aao)_3$. As stated earlier the former complex exists in the trans form (V) while the latter give cis (VI) and trans (V) forms.

We have used the above principle to probe the stereochemistry of the $Fe(aao)_3^-$ moiety. In every system studied each substituent gives rise to only one observable signal in $CDCl_3$ (Table V.4; Fig. V.3). The alkyl region of the spectra of the complex with $Ar = \text{phenyl}$ and $R = n-C_3H_7$ is shown in Fig. V.3. Every complex gives rise to a clearly observable water signal (Table V.4). This disappears on shaking the solution with D_2O .

TABLE V.4

CHEMICAL SHIFT DATA OF $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ COMPLEXES

Ar =	Compound R =	Proton type	Chemical shift ^a ppm
C_6H_5	CH_3	CH_3	2.20
		H_2O	2.50 ^b
C_6H_5	$n\text{-C}_3\text{H}_7$	$\text{CH}_3\text{CH}_2\text{CH}_2$	2.91 ^c
		$\text{CH}_3\text{CH}_2\text{CH}_2$	1.65 ^d
		$\text{CH}_3\text{CH}_2\text{CH}_2$	0.91 ^e
		H_2O	1.90 ^b
C_6H_5	$p\text{-CH}_3\text{-C}_6\text{H}_4$	$p\text{-CH}_3\text{-C}_6\text{H}_4$	2.35
		H_2O	2.20 ^b

a. Chemical shifts are from tetramethylsilane measured at 100 MHz in CDCl_3 .

b. Broad signal, vanishes on shaking the solution with a drop of D_2O .

c. Centre of a broad signal (triplet) with half height 20 Hz.

d. Centre of a sextet ($J = 7$ Hz).

e. Centre of a triplet ($J = 7$ Hz).

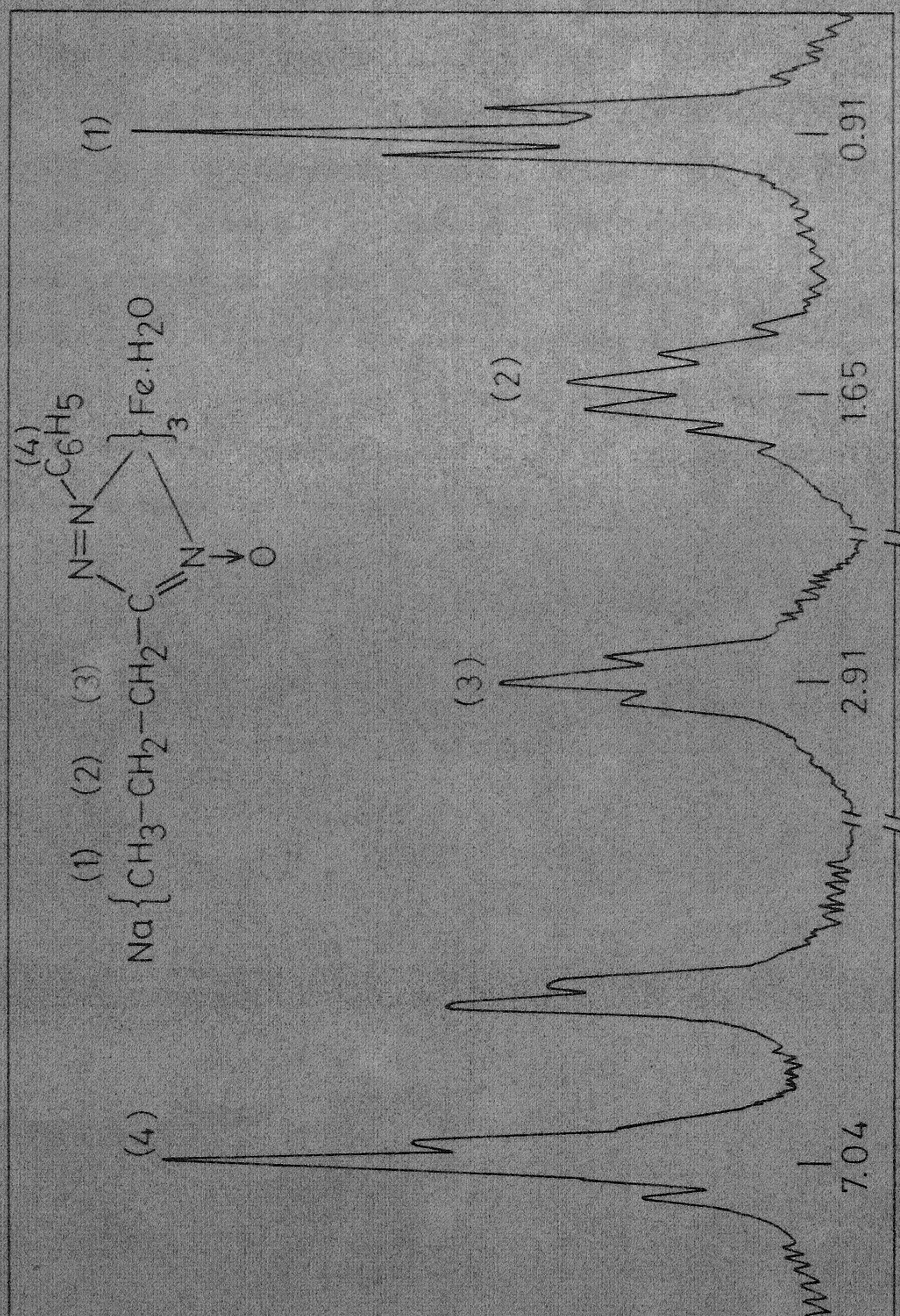
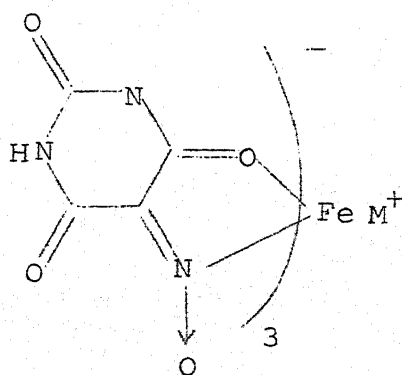
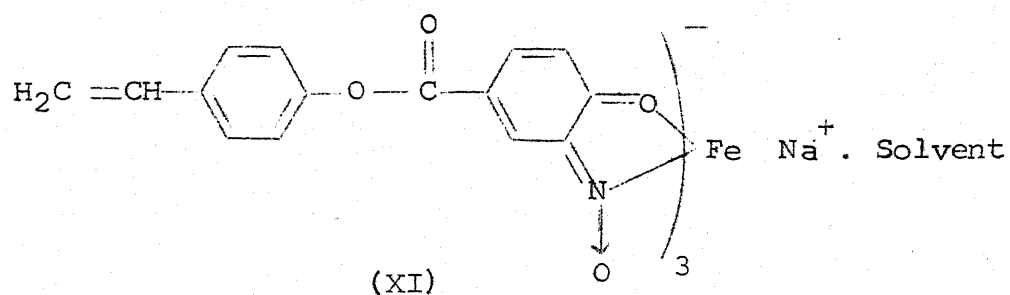


FIG. V.3 PMR SPECTRUM OF $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ ($\text{R} = n\text{-C}_3\text{H}_7$; $\text{Ar} = \text{C}_6\text{H}_5$) IN CDCl_3 .
CHEMICAL SHIFTS ARE FROM TETRAMETHYLSILANE IN PPM

The pmr spectra of $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ strongly suggest a cis structure (VI) for the Fe(aao)_3^- moiety (a nonrigid trans structure is of course not eliminated). In this connection it may be significant that the preference of iron(II) for the cis stereochemistry in anionic tris chelates of bidentate oxime ligands is well documented in several cases. Mention may be made of ferroverdin¹⁶ (XI), a green naturally occurring quinone-oxime tris complex of iron(II) and iron(II) violuret complex¹⁷ (XII). In each of these cases solvated salts of the type NaFeL_3 are readily isolated in the solid state.



e. Solution Electrical Conductivity Data: Binding of Sodium Ion

The fact that $\text{NaFe(aao)}_3\text{H}_2\text{O}$ is soluble in nonpolar solvents like benzene (infact the solubility in benzene is considerably more than that in water) strongly suggests that the sodium ion is chemically bound to the Fe(aao)_3^- moiety. This is corroborated by the observation that solutions of $\text{NaFe(aao)}_3\cdot\text{H}_2\text{O}$ in nitromethane or nitrobenzene have low conductivities at room temperature (Table V.5). The expected conductivities for 1:1 electrolytes in nitromethane and nitrobenzene respectively lie¹⁸ in the ranges 75-95 and 20-30 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. The observed conductivities clearly show that ion separation occurs only to a very limited extent in solutions of $\text{NaFe(aao)}_3\cdot\text{H}_2\text{O}$ in nitrohydrocarbons. The sodium ion evidently remains largely bound in a complexed form.

On the basis of these data alone it is not possible to make any specific suggestions about the stereochemistry and the mode of bonding of sodium. However, it is very likely that the oxygen atoms of the oxime functions and of the solvent of crystallisation are involved in coordination with sodium ion. This is schematically represented in structure XIII. Coordination of

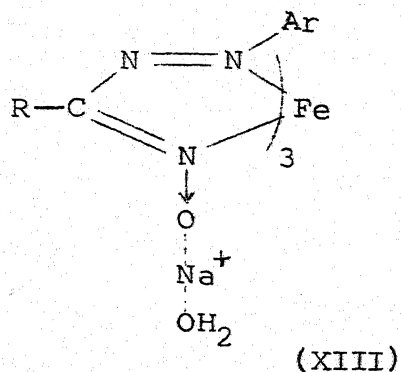


TABLE V.5

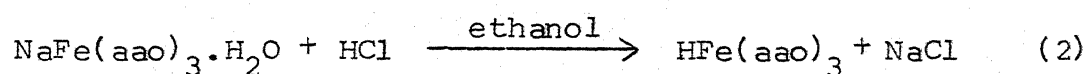
CONDUCTIVITY DATA FOR $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ COMPLEXES AT 25°C

Compound Ar =	R =	Solvent	Concentration mol. lit. ⁻¹	Λ ohm ⁻¹ .cm ² mol ⁻¹
C_6H_5	$\underline{n}\text{-C}_3\text{H}_7$	Nitrobenzene	1.8×10^{-3}	0.2
C_6H_5	$\underline{p}\text{-CH}_3\text{-C}_6\text{H}_4$	Nitrobenzene	3.7×10^{-3}	0.3
C_6H_5	$\underline{p}\text{-CH}_3\text{-C}_6\text{H}_4$	Nitromethane	1.5×10^{-3}	21.0

oxime oxygen to sodium ion is known to occur in the triclinic form of ferroverdin¹⁶ (XI). It is also noted that in 2:1 adducts of picolinic-N-oxide with sodium iodide, the sodium ions¹⁹ are believed to be coordinated to the N-oxide oxygen. A related information is that in the potassium salt of isonitrosoacetophenone, the binding of potassium ion to oxime oxygen occurs.²⁰ It will be appropriate to call $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ as a mixed complex in which the arylazooxime moiety binds both iron(II) and sodium(I).

C. System HFe(aao)_3

This is obtained by the following reaction which



was only briefly investigated. The solids are diamagnetic and have low electrical conductivity (Table V.6) in nitromethane solution. Their ir (Table V.6) and electronic spectra (Table V.6, and Fig. V.4) are closely akin to those of $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$. Evidently HFe(aao)_3 contains a proton bound to Fe(aao)_3^- . The most probable binding site is oxime oxygen. Whether the proton is bound to one oxygen or is chelated to more than one oxygen atom (intramolecularly or intermolecularly) is not certain. No clearly observable ν_{OH} frequency could be located in the region $2000\text{--}3500 \text{ cm}^{-1}$. However, a broad band of moderate intensity at $\sim 1680 \text{ cm}^{-1}$ is present in these systems. Strongly chelated O--H--O

TABLE V.6

ELECTRICAL CONDUCTIVITY, INFRARED FREQUENCIES (cm^{-1}),
 ABSORPTION MAXIMA (λ , nm) AND EXTINCTION COEFFICIENTS
 (ϵ , $\text{L.MOL}^{-1}.\text{CM}^{-1}$) OF HFe(aao)_3 COMPLEXES

Conductivity Data (Nitromethane)

Compound	Concentration (mol.lit^{-1})	Λ ($\text{ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$)
$\text{R=Ar=C}_6\text{H}_5$	1.04×10^{-3}	3
$\text{Ar=C}_6\text{H}_5$; $\text{R=p-CH}_3\text{-C}_6\text{H}_4$	9.67×10^{-4}	4

Infrared Data^a

HFe(aao)_3 $\text{R=Ar=C}_6\text{H}_5$	HFe(aao)_3 $\text{Ar=C}_6\text{H}_5$ $\text{R=p-CH}_3\text{-C}_6\text{H}_4$	Assignment
3400	3400	$\nu_{\text{O-H}}$
1603	1610	$\nu_{\text{C=N}}$
1270, 1240	1270, 1240	$\nu_{\text{N-O}}$
738, 765, 688	630, 760, 690	Out-of-plane δ_{CH}

Electronic Spectral Data^b

Compound	$\lambda(\epsilon)$
$\text{R=Ar=C}_6\text{H}_5$	560(10,131); 413(15,743)
$\text{Ar=C}_6\text{H}_5$; $\text{R=p-CH}_3\text{-C}_6\text{H}_4$	570(11,676); 420(16,523)

a. Infrared spectra were run in KBr discs.

b. Electronic spectra were run in chloroform solutions.

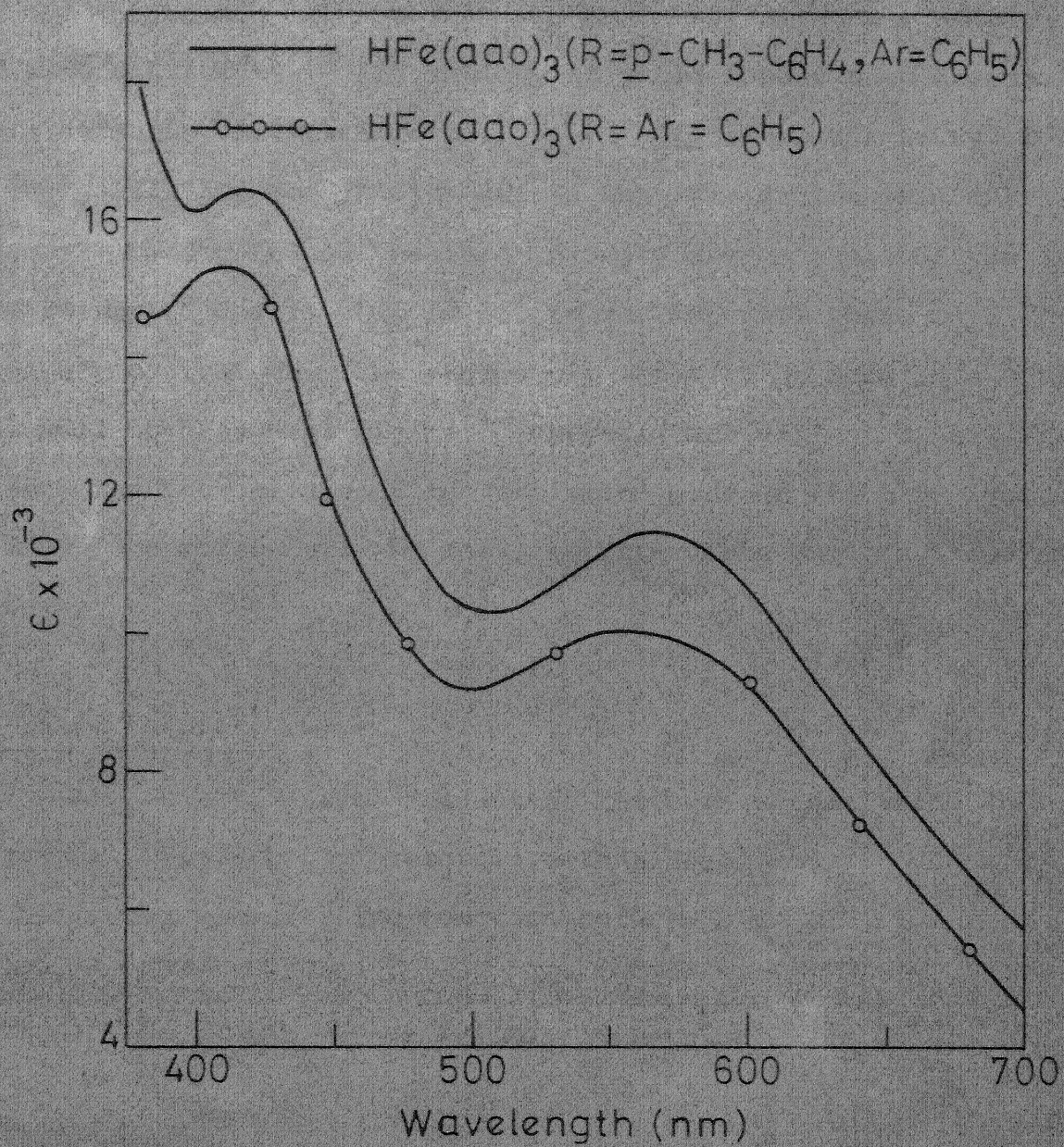
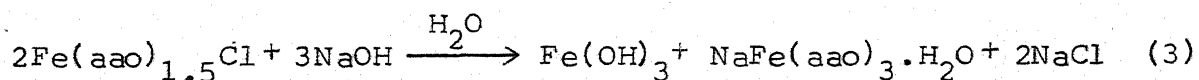


FIG. V.4 ELECTRONIC SPECTRA IN CHLOROFORM

groups (as present in bis-dimethylglyoximate complexes) are known to show bending vibrations in the region $1600-1800\text{ cm}^{-1}$, and the stretching vibration at $2200-2400\text{ cm}^{-1}$ are observed with difficulty.²² By analogy it would appear that HFe(aao)_3 has a strongly chelated proton. In the cis stereochemistry of Fe(aao)_3^- (VI) the possibility exists that the proton is simultaneously bonded to all the three oximate oxygen atoms of the same Fe(aao)_3^- unit. This is not to say that all three O--H bonds are equivalent. The proton may actually be held in a potential well with several minima. However, this may not at all represent the true nature of the chelation present which may very well be intermolecular. We shall not speculate on this issue any further.

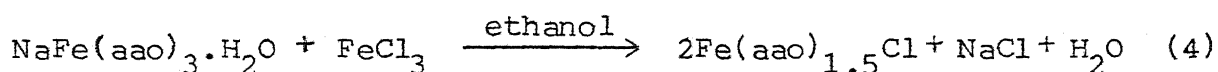
D. System $\text{Fe(aao)}_{1.5}\text{Cl}$

This is the initial product of reaction of Haao with FeCl_3 in ethanol (Fig.V.1). On reaction with aqueous sodium hydroxide the following quantitative reaction occurs:



One mole of Fe(OH)_3 is rejected per two moles of $\text{Fe(aao)}_{1.5}\text{Cl}$. Since $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ is formed so readily, it would appear that $\text{Fe(aao)}_{1.5}\text{Cl}$ has at least half of the iron in bivalent state. Rejection of Fe(OH)_3 under alkali attack does not prove the

initial presence of iron(III), since aerial oxidation may occur under the reaction conditions. However, careful experiments under oxygen free nitrogen atmosphere also led to the generation of $\text{Fe}(\text{OH})_3$. It does appear that some of the iron in $\text{Fe}(\text{aao})_{1.5}\text{Cl}$ is present in the oxidation state +3. The reconstitution of $\text{Fe}(\text{aao})_{1.5}\text{Cl}$ from $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ by the reaction (4) provides



further evidence in favour of the postulated presence of both iron(II) and iron(III) in the probable ratio 1:1. It would also appear that iron(II) is present in the form of the tris chelate $\text{Fe}(\text{aao})_3^-$.

a. Bulk Magnetic Susceptibility Data

The $\text{Fe}(\text{aao})_{1.5}\text{Cl}$ systems are strongly paramagnetic showing the presence of iron in the high-spin configuration. Unlike $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$, this system gives ill defined pmr spectra with very broad lines showing the presence of fast relaxation characteristic of paramagnetic systems. The bulk susceptibility of several $\text{Fe}(\text{aao})_{1.5}\text{Cl}$ species were measured both in the solid state and in chloroform solution. Data are presented in Table V.7. The magnetic moment is found to be ~ 4.2 BM per iron atom. However, assuming a doubled formula weight i.e., $[\text{Fe}(\text{aao})_{1.5}\text{Cl}]_2$ and assuming that one iron atom is present in the low-spin +2

TABLE V.7

MAGNETIC SUSCEPTIBILITY DATA OF $\text{Fe}(\text{aao})_{1.5}\text{Cl}$ COMPLEXES IN SOLID STATE AND
IN CHLOROFORM SOLUTION

Compound Ar = R =	Temp. $^{\circ}\text{C}$	$\chi_g \times 10^6$	$\chi_F \times 10^6$ ^a	$\mu_{\text{eff}}(\text{BM})$ ^a	$\chi_M \times 10^6$ ^b	$\mu'_{\text{eff}}(\text{BM})$ ^b
<u>SOLID STATE</u>						
C_6H_5 $\text{n-C}_3\text{H}_7$	28.5	18.74	7175	4.17	14350	5.90
C_6H_5 C_6H_5	27	17.17	7475	4.25	14950	6.01
C_6H_5 $\text{p-CH}_3\text{C}_6\text{H}_4$	28 78	15.86 13.54	7309 6223	4.21 4.19	14619 12446	5.95 5.94
<u>CHLOROFORM SOLUTION</u>						
C_6H_5 $\text{n-C}_3\text{H}_7$	28	18.95	7255	4.19	14510	5.93
C_6H_5 C_6H_5	29	16.76	7294	4.21	14589	5.96
C_6H_5 $\text{p-CH}_3\text{C}_6\text{H}_4$	28.5	15.49	7455	4.25	14190	5.87

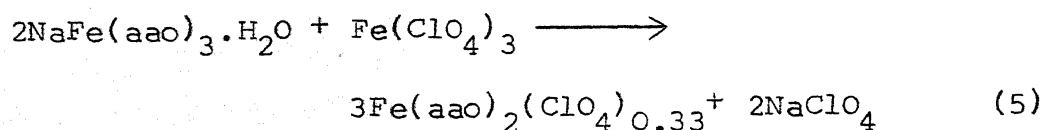
a. χ_F is the corrected susceptibility calculated using the formula $\text{Fe}(\text{aao})_{1.5}\text{Cl}$ and μ is the magnetic moment based on this.

b. μ' is computed using the formula weight $\text{Fe}_2(\text{aao})_3\text{Cl}_2$ and assuming that only one iron atom is paramagnetic and relationship between μ and μ' is $\mu' = \frac{1}{\sqrt{2}}\mu$.

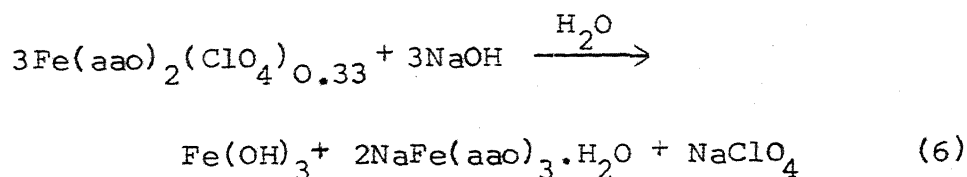
oxidation state, the magnetic moment of the other iron atom (Table V.7) turns out to be ~ 5.9 BM. This value is in line with a high-spin d^5 configuration. The magnetic data are thus consistent with the presence of low-spin iron(II) and high-spin iron(III) in the molar ratio 1:1 in $\text{Fe(aao)}_{1.5}\text{Cl}$.

b. Clue to Molecular Nature: The Case of $\text{Fe(aao)}_2(\text{ClO}_4)_{0.33}$

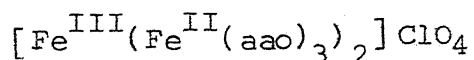
The first clue to the actual nature of $\text{Fe(aao)}_{1.5}\text{Cl}$ was obtained while investigating the species $\text{Fe(aao)}_2(\text{ClO}_4)_{0.33}$. This species was initially obtained by a direct reaction between iron(II) perchlorate and HaaO. We were hoping to obtain tetragonal systems of the type $\text{Fe(aao)(HaaO)(ClO}_4)$. Such a system was never obtained. The odd species $\text{Fe(aao)}_2(\text{ClO}_4)_{0.33}$ resulted instead. In course of synthesis at least part of the iron has got oxidised to the +3 state. We later observed that the same species could be obtained by reacting iron(III) perchlorate (1 mol) with $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ (2 mol) (Fig. V.1). This synthetic reaction is:



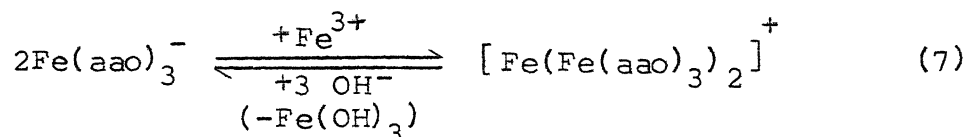
On the other hand the perchlorate quantitatively loses 1/3 of its iron content as $\text{Fe}(\text{OH})_3$ and is converted to $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$, on reaction with sodium hydroxide according to the reaction:



The above observations led us to suspect that $\text{Fe}(\text{aao})_2(\text{ClO}_4)_{0.33}$ may contain iron(III) bound in some way to $\text{Fe}(\text{aao})_3^-$ with perchlorate balancing the extra positive charge as in



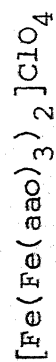
The weight of this formula is equal to that of $3\text{Fe}(\text{aao})_2(\text{ClO}_4)_{0.33}$. It is readily seen that with the above formulation the reaction (5) and (6) can be rationalised as:



The electrical conductivity (calculated on formula $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$) in nitromethane solution (20°C) is in excellent agreement with 1:1 electrolytic behaviour¹⁸ (Table V.8). The powder magnetic susceptibility of one system viz., $\text{R}=\text{Ar}=\text{C}_6\text{H}_5$ was determined (Table V.8). The results show that system contains five unpaired electrons. This is readily understandable if one assumes that the iron(II) atoms are low-spin (a fully justified assumption in view of the results on $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$) while the iron(III) atom is high-spin.

TABLE V.8

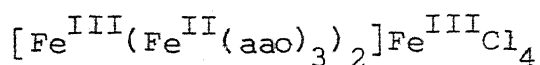
ELECTRICAL CONDUCTIVITY AND MAGNETIC DATA OF



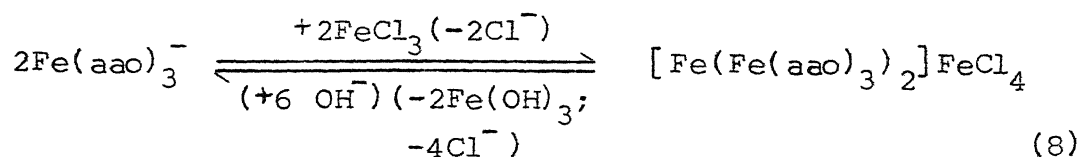
Conductivity Data (Nitromethane)			
Compound	Concentration (mol.lit. ⁻¹)	Λ (ohm ⁻¹ .cm ² .mol ⁻¹)	
R = Ar = C ₆ H ₅	7.345 x 10 ⁻⁴	76	
Ar = C ₆ H ₅ ; R = p-CH ₃ -C ₆ H ₄	3.585 x 10 ⁻⁴	76	

Magnetic Data (Compound: R = Ar = C ₆ H ₅)			
Temp. °C	$\chi_g \times 10^6$ (cgs unit)	$\chi_M \times 10^6$ (cgs unit)	μ_{eff} (BM)
21.5	8.3	14167	5.80

With these informations at hand, a reexamination of the properties of $\text{Fe}(\text{aao})_{1.5}\text{Cl}$ described earlier (and spectral properties to be described later) led us to examine the formulation:



which has the same formula weight as $4\text{Fe}(\text{aao})_{1.5}\text{Cl}$. The difference between the 'perchlorate' and the 'chloride' lies in the replacement of ClO_4^- by FeCl_4^- in the anionic part. Both have the same trinuclear cation. The magnetic data of Table V.8 are in full agreement with such a formulation. Of the four iron atoms two (both iron(II) are present in the cation) are low-spin and two (both are iron(III); one is present in the cation and one in the anion) are high-spin (d^5). Only half of the iron atoms thus contribute to paramagnetic susceptibility. The reactions (2) and (3) can then be rationalised



The electrical conductivity data are in full agreement with the above formula (Table V.9). The $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ system is a well behaved 1:1 electrolyte.¹⁸

TABLE V.9

ELECTRICAL CONDUCTIVITY OF $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ COMPLEXES AT 25°C

Compound Ar =	R =	Solvent	Concentration (mol.lit ⁻¹)	Λ (ohm ⁻¹ .cm ² .mol ⁻¹)
C ₆ H ₅	C ₆ H ₅	Nitromethane	1.88 x 10 ⁻³	76
C ₆ H ₅	p-CH ₃ -C ₆ H ₄	Nitromethane	1.47 x 10 ⁻³	76
C ₆ H ₅	p-CH ₃ -C ₆ H ₄	Nitrobenzene	3.37 x 10 ⁻³	18

c. Infrared Data

In the region $4000\text{--}600\text{ cm}^{-1}$ the infrared spectra of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ ($\text{X} = \text{ClO}_4, \text{FeCl}_4$) are closely akin to that of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ except for small differences in frequencies and the relative intensities of bands. (Of course the ν_{OH} band is absent in the former system, which has additional perchlorate bands for the case $\text{X} = \text{ClO}_4$). This corroborates the presence of bound $\text{Fe}(\text{aao})_3^-$ moiety in both systems.

Among the $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ species, the spectrum (region $4000\text{--}600\text{ cm}^{-1}$), of $\text{X}^- = \text{ClO}_4^-$ is virtually superposable on the spectrum of $\text{X}^- = \text{FeCl}_4^-$ except for the ClO_4^- absorptions which appear only in the former complex. A representative example is shown in the Fig. V.5. Selected frequencies are set out in Table V.10.

Of the four perchlorate vibrations only ν_3 and ν_4 are ir active.²³ $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ shows ν_3 and ν_4 bands at ~ 1085 and $\sim 630\text{ cm}^{-1}$ respectively (Fig. V.5 & Table V.10). The ν_3 band shows no sign of splitting and the observed spectra are in full agreement with the presence of ionic ClO_4^- in the crystal lattice.

The spectra in the low frequency region ($500\text{--}300\text{ cm}^{-1}$) are displayed in the Fig. V.6 for $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ and $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ ($\text{X} = \text{ClO}_4, \text{FeCl}_4$) where the ligand has $\text{R} = \text{Ar} = \text{C}_6\text{H}_5$ or $\text{R} = \text{p-CH}_3\text{-C}_6\text{H}_4$ and $\text{Ar} = \text{C}_6\text{H}_5$. The following observations are in order:

(1) $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ does not show any major bands in this region (the same is true of the free ligands whose ir spectra

TABLE V.10

SELECTED INFRARED STRETCHING FREQUENCIES^{a, b} (cm^{-1})

$[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ R = Ar = C_6H_5	$[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ Ar = C_6H_5 ; R = $\text{p-CH}_3\text{-C}_6\text{H}_4$	$[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ R = Ar = C_6H_5	$[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ Ar = C_6H_5 ; R = $\text{p-CH}_3\text{-C}_6\text{H}_4$	Assignment
1585	1605	1585	1605	$\nu_{\text{C}=\text{N}}$
1240, 1202	1245, 1205	1240, 1200	1245, 1205	$\nu_{\text{N}-\text{O}}$
-	-	1085	1085	$\nu_3 \text{ClO}_4$
-	-	630	635	$\nu_4 \text{ClO}_4$
762, 737, 690	830, 760, 690	770, 760, 690	830, 760, 690	Out-of-plane δ_{CH}
432	432	428	430	$\nu_{\text{Fe(III)}-\text{O}}$
385	376	-	-	$\nu_3 \text{Fe-Cl}$

a. All the spectra in the region $4000\text{-}600\text{ cm}^{-1}$ were run in KBr discs.b. Below 600 cm^{-1} spectra were taken in nujol mull.

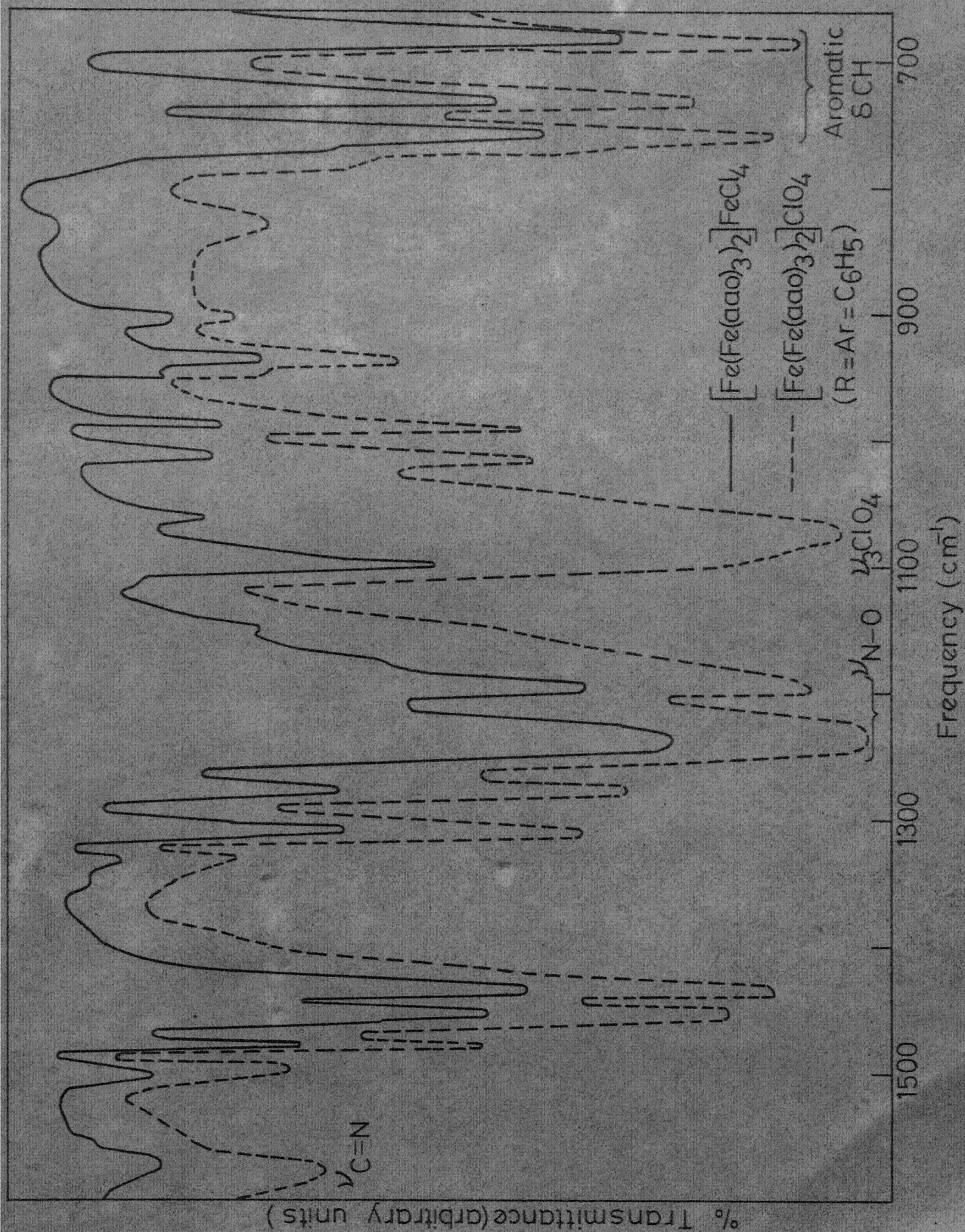


FIG. V.5 INFRARED SPECTRA OF $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ ($\text{X} = \text{FeCl}_4, \text{ClO}_4$) COMPLEXES

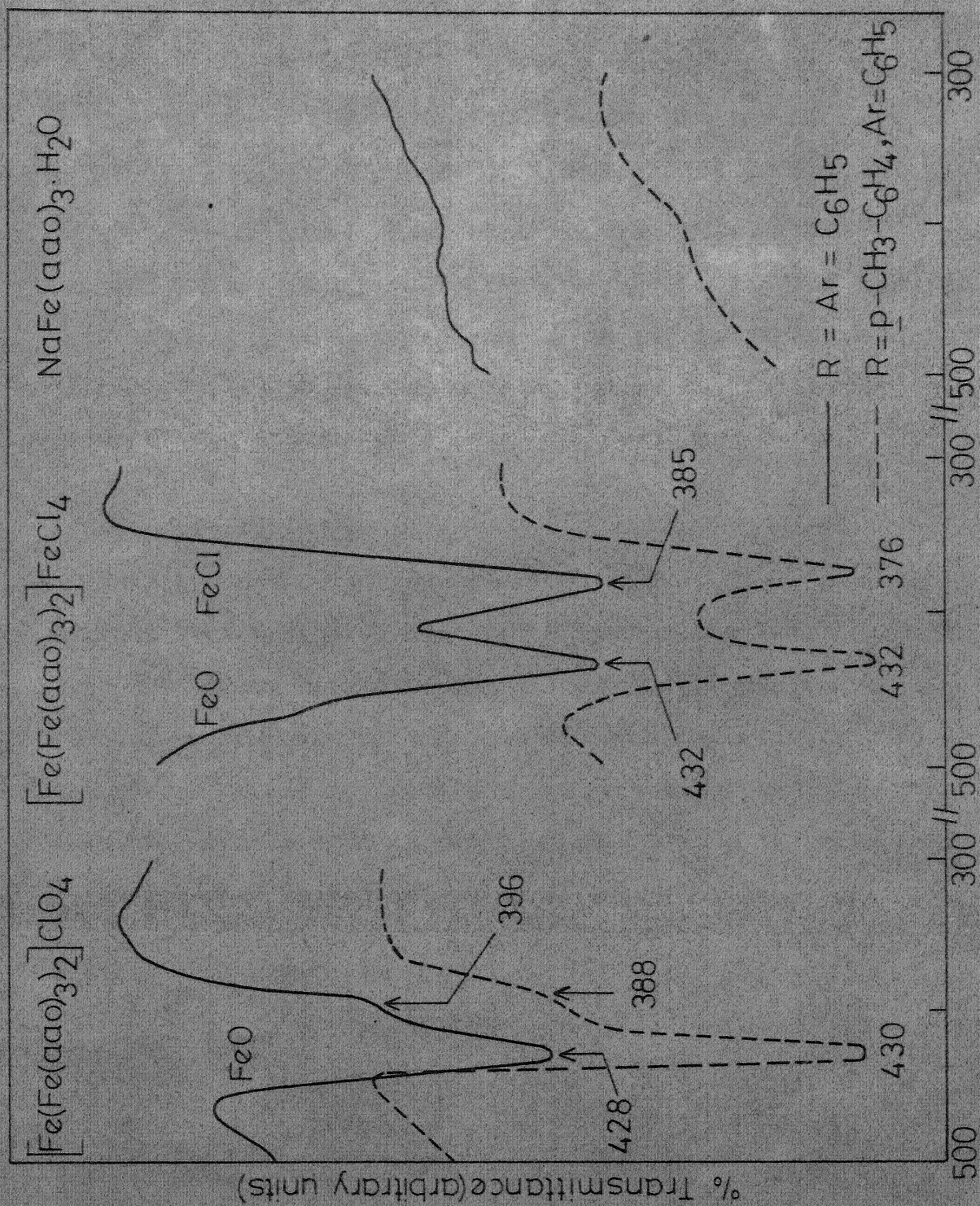


FIG. V.6 Fe-O AND Fe-Cl STRETCHING FREQUENCIES (CM⁻¹)

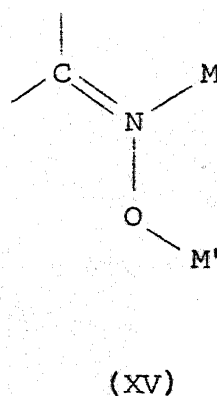
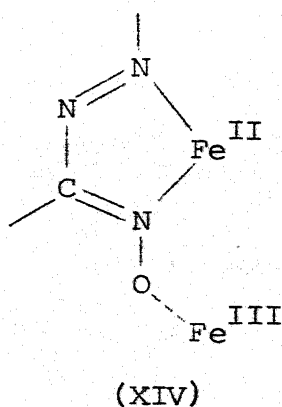
were also run). Any Fe(II)-N and Na-O frequency present in this region is too weak to be observed.

(2) $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ shows a strong band at 385 cm^{-1} . This band which is absent in the corresponding perchlorate is assigned²⁴ to ν_3 (essentially Fe-Cl stretch) of FeCl_4^- .

(3) $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ exhibits a band at $\sim 430\text{ cm}^{-1}$ with a shoulder at $\sim 390\text{ cm}^{-1}$. A corresponding band is also observed in $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ at 432 cm^{-1} . We believe that this is due to the Fe(III)-O stretch arising out of the bonding of Fe(III) to oxime oxygen atoms. This point is considered below:

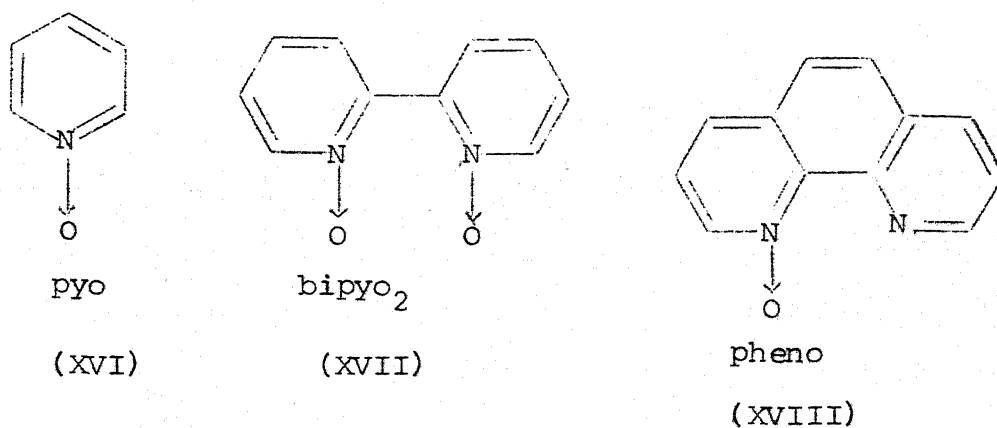
d. Binding of Iron(III)

In view of the results described so far, it is reasonable to propose that in the mixed valence species the $\text{Fe}(\text{aao})_3^-$ moiety has the same gross structure as in $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$. Since $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]^+$ behaves as a single cation (conductivity data), the iron(III) atom is evidently bound to the $\text{Fe}(\text{aao})_3^-$ units. The most reasonable mode of bonding could be one in which iron-(III) is attached to the oxygen atoms of the oxime groups shown



in structure XIV. In XIV, the oxime function is acting as a bridging group between Fe(II) and Fe(III). This is one instance (a very unusual one) of the more general case^{25, 26} (XV). This structural type (XV) has been established for $M=M'=\text{Cu}$, Ni , Pd ; $M=\text{Cu}$, $M'=\text{Ni}$ etc.

In XIV, the bonding to Fe(III) is essentially the bonding of a N-oxide oxygen (sp^2N). Pseudooctahedral iron(III) complexes of neutral monodentate or bidentate N-oxides are well known^{27, 28} e.g., $[\text{Fe}(\text{pyo})_6](\text{ClO}_4)_3$ (ref. 29), $[\text{Fe}(\text{bipyo}_2)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ (ref. 30), and $[\text{Fe}(\text{pheno})_3](\text{NO}_3)_2$ (ref. 31). In the former



two species the coordination sphere is high-spin FeO_6 . In the third species the FeO_3N_3 coordination sphere shows low-spin — high-spin equilibrium. In strictly octahedral MO_6 only one degenerate ir active M-O stretch is expected. When the symmetry is lower, two M-O bands are often observed²³ (removal of degeneracy). The N-oxide complexes of iron(III) (FeO_6 coordination sphere) show one or two ir bands assignable to Fe-O, e.g.,

$[\text{Fe}(\text{pyo})_6](\text{ClO}_4)_3$ 383 cm^{-1} (strong) (ref. 29)

$[\text{Fe}(\text{bipyo}_2)_3](\text{ClO}_4)_3$ 408 cm^{-1} (strong), (ref. 30)
 377 (shoulder,
 medium).

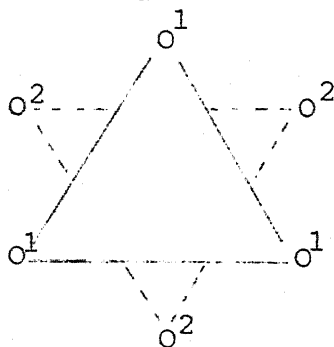
In $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$, the band at $\sim 430 \text{ cm}^{-1}$ (together with the shoulder at $\sim 390 \text{ cm}^{-1}$) (Fig. V.6) is assigned to Fe(III)-O stretch. The oxime oxygen of negatively charged $\text{Fe}(\text{aao})_3^-$ moiety binds to iron(III) more strongly than do the neutral N-oxide ligands.

It is possible to suggest a probable stereochemistry for the iron(III) atom on the basis of general considerations, model building and experimental results.

In molecular systems iron(III) in combination with oxygen ligands usually exhibits grossly octahedral geometry. The FeO_6 coordination sphere is always high-spin (tetrahedral $\text{Fe}(\text{III})-\text{O}_4$ is known to exist quite commonly in oxide lattices e.g., in orthoclase feldspar (KAlSi_3O_8) containing a small percentage of Fe^{3+} in place of Al^{3+} (ref. 32)).

In $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]^+$, an octahedral stereochemistry on iron(III) can be readily achieved from cis stereochemistry (structure VI) of $\text{Fe}(\text{aao})_3^-$ (compare with the case of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$). In this geometry, the three oxime functions span the same face of the iron(II) octahedron (VI). The lone pairs on the three oxime oxygen atoms (roughly sp^3 hybridised) are correctly directed to bind to the three corners of a face of the iron(III) octahedron.

A second cis $\text{Fe}(\text{aao})_3^-$ unit can then similarly bind to another face completing the iron(III) octahedron. This is schematically shown in (XIX), in which the oxygen atoms coming from the same $\text{Fe}(\text{aao})_3^-$ unit carry the same number on the top. A clearer view of this structure can be obtained from the drawing in Fig. V.7.



(XIX)

The $\text{Fe}(\text{II})$ - $\text{Fe}(\text{III})$ - $\text{Fe}(\text{II})$ chain is essentially linear (lying on an idealised three-fold axis) in this structure.

The observed high-spin character of iron(III) is consistent with this structure (FeO_6 coordination sphere). In such a structure the strict symmetry of FeO_6 can in no case be O_h . The actual symmetry may be quite low depending on the distortions present. In this context it is significant that two Fe-O stretches (band at $\sim 430 \text{ cm}^{-1}$ and shoulder at $\sim 390 \text{ cm}^{-1}$) are observed (Fig. V.6).

f. Electronic Spectra

The electronic spectra of several $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ ($\text{X} = \text{FeCl}_4$, ClO_4) species were run in chloroform solution. Data are presented

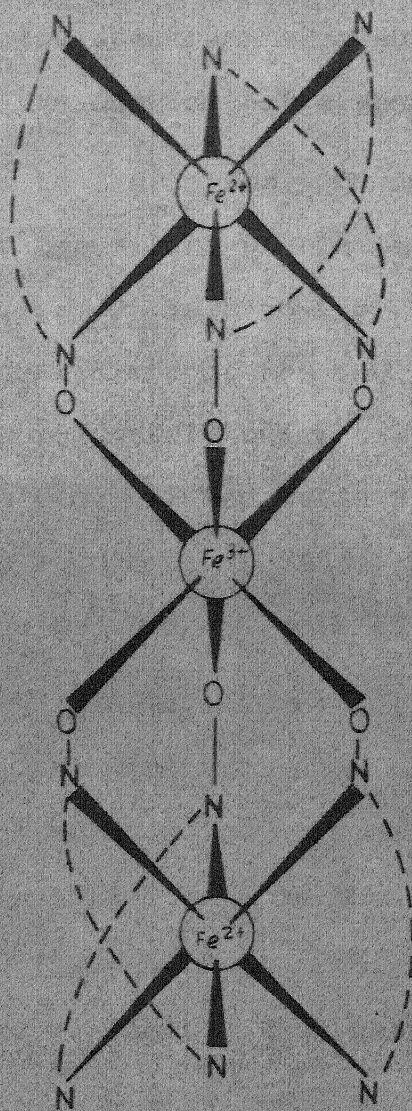


FIG. V.7 BINDING OF IRON(III) IN $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$
 ($\text{X} = \text{ClO}_4, \text{FeCl}_4$)

in Table V.11 and Fig. V.8. No other bands are observed above 600 nm. Two characteristic bands are seen at ~ 600 nm and ~ 470 nm. Both bands correspond to allowed transitions. For a given R and Ar group, the spectrum is independent of X, showing that both transitions are due to $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]^+$.

It is reasonable to assign the ~ 600 nm band to the metal \rightarrow ligand charge transfer transition within the $\text{Fe}(\text{aao})_3^-$ unit (compare with $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$: Section V.B). It is significant that the extinction coefficient of the ~ 600 nm band in $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ is approximately twice that of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ (compare Fig. V.8 with Fig. V.2 and Table V.11 with Table V.3). This is expected since each mole of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ and $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ contains two and one mole of $\text{Fe}(\text{aao})_3^-$ respectively.

The origin of the band at ~ 470 nm is less certain. However, it appears that it has the same origin as the ~ 400 nm band of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$. This band is quite sensitive to the cation to which $\text{Fe}(\text{aao})_3^-$ is bound. For example when the cation is H^+ (Section C), this band is at ~ 420 nm. This shifts to ~ 440 nm, when the cation Ni^{2+} (see below). Thus there is a systematic shift to lower energy in the order $\text{Na}^+ > \text{H}^+ > \text{Ni}^{2+} > \text{Fe}^{3+}$.

High-spin iron(III) can exhibit only spin-forbidden ligand field transitions. Grossly octahedral FeO_6 moiety is known to show³² several such transitions of very low intensity in the range 790-360 nm. $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ may be expected to show similar transitions. When $\text{X} = \text{FeCl}_4$, additional spin-forbidden transitions

TABLE V.11

ABSORPTION MAXIMA (λ , nm) AND EXTINCTION COEFFICIENTS (ϵ , L.MOL⁻¹.CM⁻¹) OF [Fe(Fe(aao)₃)₂]_x (X = FeCl₄, ClO₄) COMPLEXES IN CHLOROFORM SOLUTIONS

Compound	$\lambda(\epsilon)$
<hr/>	
[Fe(Fe(aao) ₃) ₂] ₂ FeCl ₄	
R = Ar=C ₆ H ₅	600(22,754); 460(37,724); 355(49,400) sh
Ar=C ₆ H ₅ ;	
R=p-CH ₃ -C ₆ H ₄	600(23,400); 480(34,900); 355(51,866) sh.
<hr/>	
[Fe(Fe(aao) ₃) ₂] ₂ ClO ₄	
R = Ar=C ₆ H ₅	595(26,193); 460(44,000).
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sh, Shoulder,	

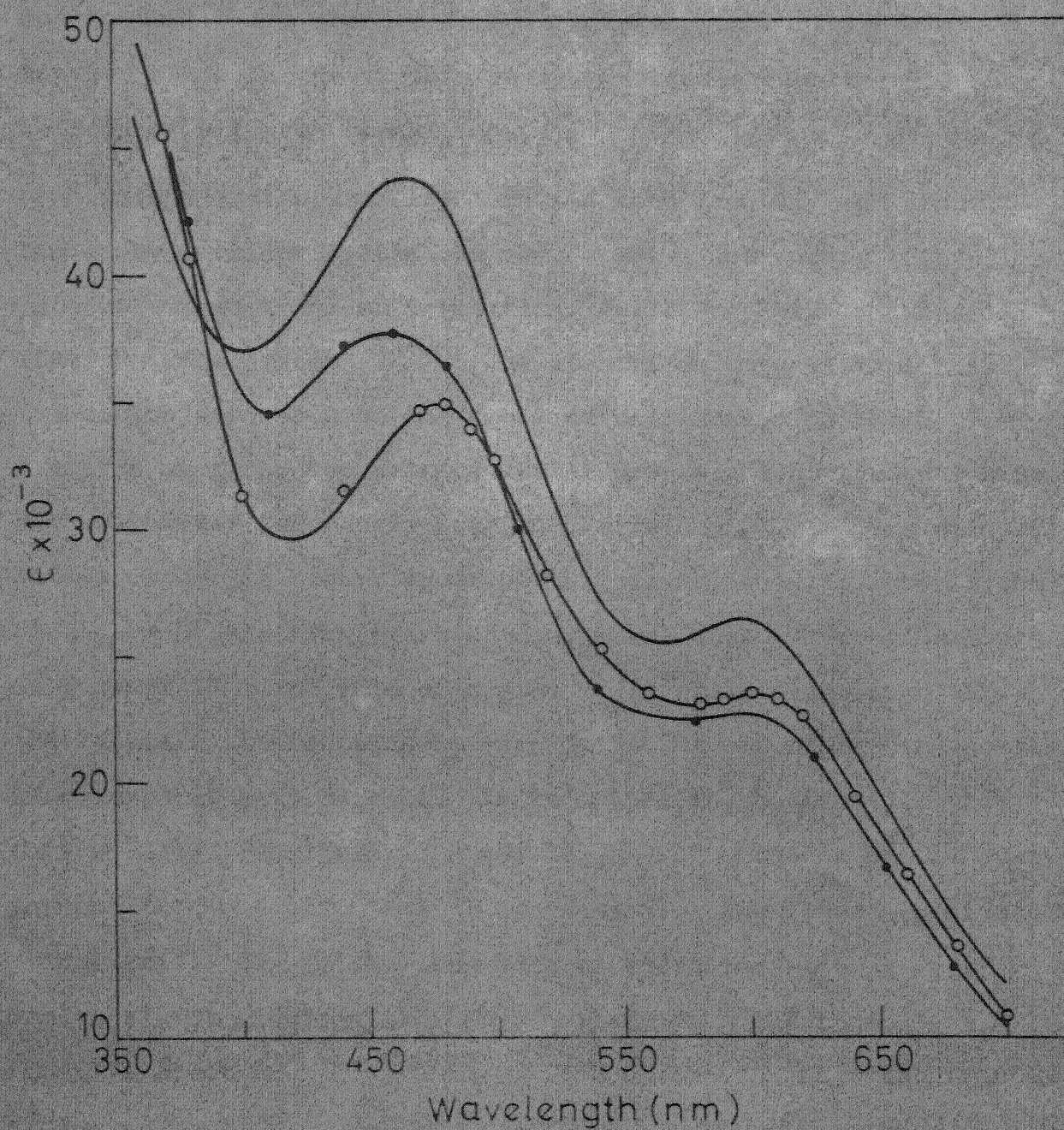


FIG. V.8 ELECTRONIC SPECTRA OF $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ ($\text{R}=\text{Ar}=\text{C}_6\text{H}_5$) (—), $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ ($\text{R}=\text{p-CH}_3\text{-C}_6\text{H}_4$; $\text{Ar}=\text{C}_6\text{H}_5$) (—●—●—) AND $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ ($\text{R}=\text{Ar}=\text{C}_6\text{H}_5$) (—○—○—) IN CHLOROFORM

due to FeCl_4^- are also expected. However, the existence of intense bands in the visible region precludes experimental observations of all such transitions.

Since $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ contain both iron(II) and iron(III) linked by a bridge system one may expect a low-energy intervalence charge transfer transition: $\text{Fe(II)} \rightarrow \text{Fe(III)}$ (Class II mixed valence system).³³⁻³⁶ The absorption intensity of this transition depends upon the small delocalisation of the optical electron over the two valence states. When the two valence sites are well-separated (as is true in $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$), the delocalisation occurs via higher order perturbation involving $\text{M} \rightarrow \text{ligand}$, $\text{ligand} \rightarrow \text{M}'$ electron transfer configurations. An ideal example of a class II mixed valence system is Prussian blue which like $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ contains low-spin iron(II) and high-spin iron(III) in octahedral environments. In this case the $t_{2g}(\text{Fe(II)}) \rightarrow t_{2g}(\text{Fe(III)})$ transition is observed at ~ 680 nm. The band is very intense ($\epsilon \sim 8000$ in colloidal suspension). The linear cyanide bridge $\text{Fe(II)}-\text{C}\equiv\text{N}-\text{Fe(III)}$ provides an effective pathway (via π -orbitals) for electron (t_{2g}) delocalisation.³⁶ Further each iron(II) electron can jump to any one of the six adjacent iron(III) sites.

In $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$, we have not been able to locate any distinctive intervalence band. The delocalisation of the t_{2g} electrons via the N-O bridge in the proposed stereochemistry (Fig. V.7) will be much less than that through CN bridge in

Prussian blue. Then there is a very strong iron(II) \rightarrow ligand transition centred at ~ 600 nm. The intensity of this band is quite large even at 700 nm ($\epsilon \sim 11,000$) and beyond (Fig. V.8). These factors may be responsible for the failure to observe the intervalence band.

g. Some Related Species

Preliminary results on two systems will be briefly stated here, since these have some bearings on the structural problem at hand.

Attempted synthesis of the bromide analogue of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2] \cdot \text{FeCl}_4$ (by replacing FeBr_3 for FeCl_3 in the synthetic method) led to a product which had all the properties expected of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{Br}$. In the region $500\text{--}300\text{ cm}^{-1}$ it shows only the Fe-O stretch ($\sim 420\text{ cm}^{-1}$).

$\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ reacts with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ethanol to give a non-electrolytic product which can be formulated as $\text{Ni}[\text{Fe}(\text{aao})_3]_2$. Apart from showing the intense $\text{Fe}(\text{aao})_3^-$ bands ($\sim 600\text{ nm}$; 440 nm) it exhibits a weak broad band at $\sim 1390\text{ nm}$ which may be due to the presence of nickel in a very weak octahedral ligand field (ν_1 transition). Our speculation is that its structure is similar to that of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]^+$ (Fe^{3+} replaced by Ni^{2+}).

E. EPR Spectra

The room temperature powder epr spectra of two $[\text{Fe}(\text{Fe}(\text{aao})_3)_2] \cdot \text{ClO}_4$ complexes are displayed in Fig. V.9. The most characteristic feature is an absorption with an apparent g value (g') of ~ 4.3 . This strongly suggests a rhombic geometry for the FeO_6 coordination sphere. The system $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{Br}$ behaves similarly (Fig. V.10).

The polycrystalline epr spectra of rhombically distorted octahedral high-spin $\text{Fe}^{3+}(\text{d}^5)$ have been the subject of many investigations.³⁷⁻⁴³ The $S = \frac{5}{2}$ state splits into three Krammer doublets ($S_z = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$). The eigen functions are actually a mixture of the three doublets, the extent of mixing depends on the parameter $\lambda = E/D$. The spin Hamiltonian usually used to fit the spectra is

$$\mathcal{H}_S = g \beta H \cdot \bar{S} + D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2) \quad (9)$$

The parameter λ is a measure of the rhombic character of the crystalline environment. The maximum possible (i.e., perfect) rhombic symmetry in the crystalline field occurs as $\lambda = \frac{1}{3}$ ($\lambda = 0$ or 1 corresponds to perfect axial symmetry). For the $S = \frac{5}{2}$ system six energy levels are present in a magnetic field (levels 1, 2, 3, 4, 5, 6 in order of increasing energy). A sizable number of transitions are thus possible and are often observed spread over a wide range of field (typically 600-8000 G in the X-band).

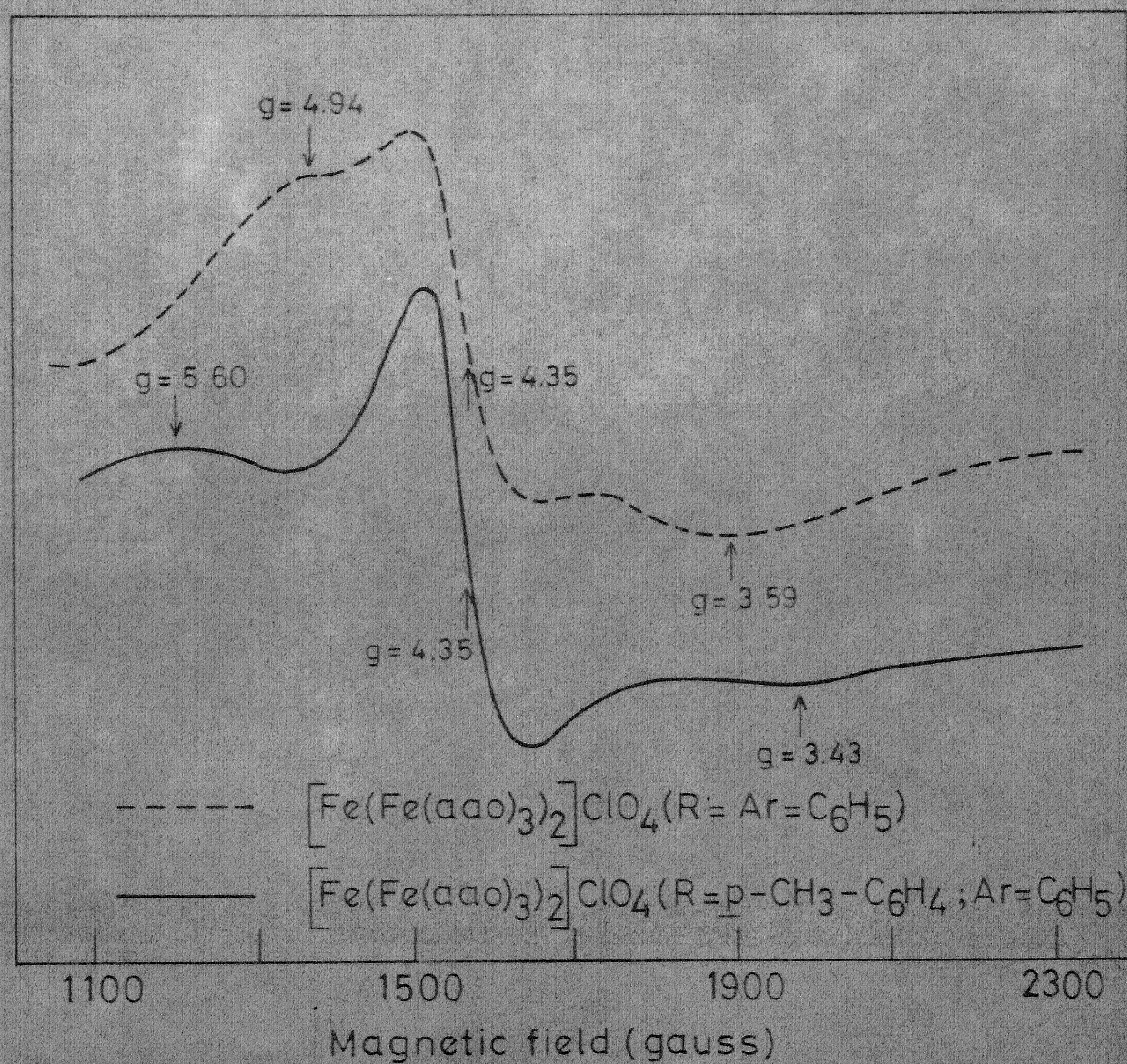


FIG. V. 9 POWDER ELECTRON SPIN RESONANCE SPECTRA

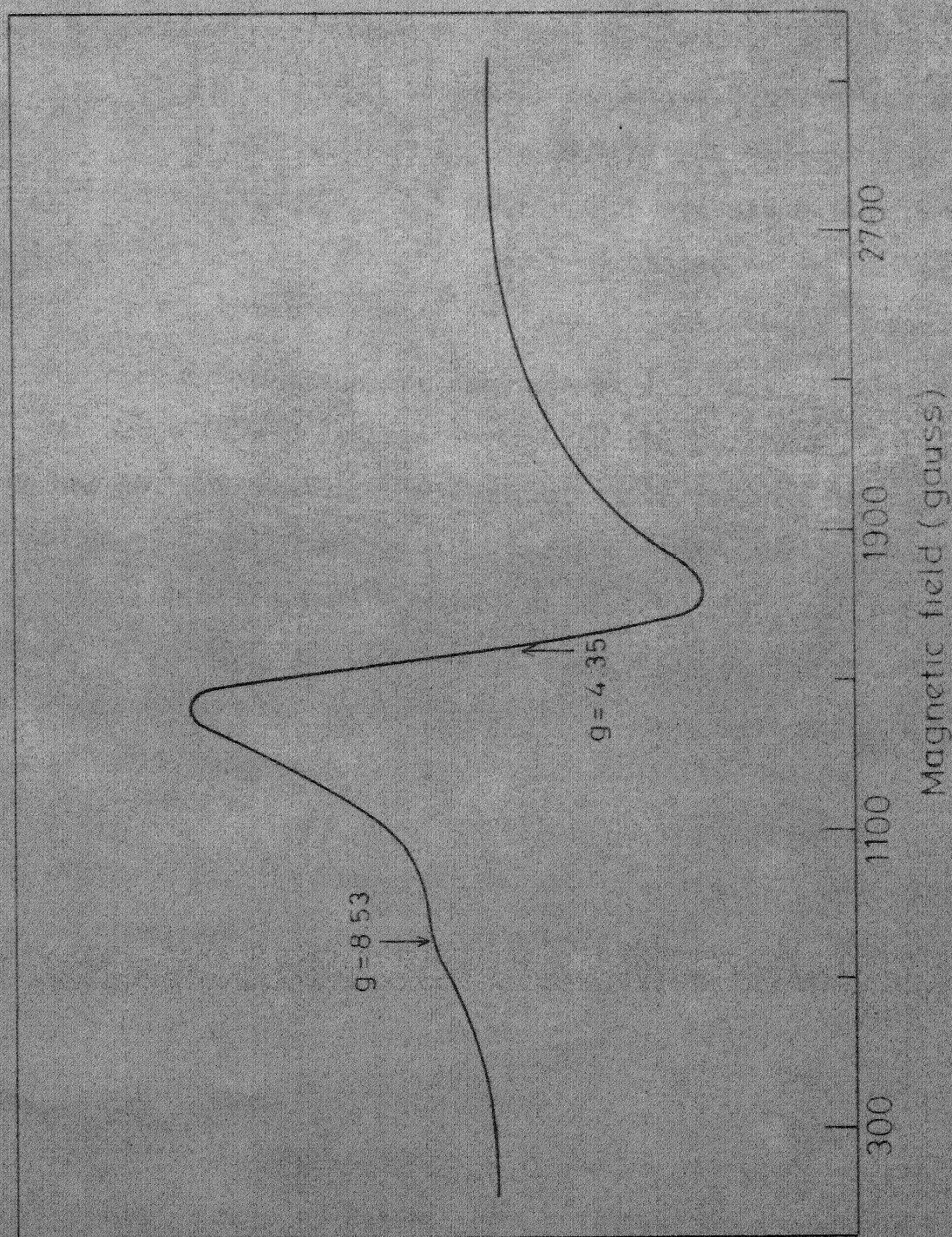


FIG. V.10 POWDER ELECTRON SPIN RESONANCE SPECTRUM OF $[\text{Fe}(\text{Fe}(\mu\text{-oxo})_3)_2]\text{Br}$
 ($\text{R} = \text{Ar} = \text{C}_6\text{H}_5$)

However, the most intense and therefore the most characteristic of all is a transition (level $3 \rightarrow 4$) with $g' \sim 4.3$. This absorption is isotropic at $\lambda = \frac{1}{3}$. Deviation of λ from $\frac{1}{3}$ brings in anisotropy which is reflected in the experimental spectrum as a broadening or splitting^{38,39,42} of the $g' \sim 4.3$ transition. The $g' \sim 4.3$ absorption has been used as a signature of perfect or nearly perfect rhombic symmetry in pseudooctahedral Fe^{3+} species.

Our comment that the epr spectrum of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]_2\text{X}$, ($\text{X} = \text{ClO}_4, \text{Br}$) suggests a rhombic geometry for the FeO_6 coordination sphere has to be viewed in the light of above discussion. The observed spectra are comparable to those of other rhombic FeO_6 systems such as sideramines⁴⁰ and Ferrichrome-A (ref. 39). The $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]_2 \cdot \text{FeCl}_4$ again shows an absorption at $g' \sim 4.3$ (Fig. V.11). This absorption is partially superposed on a more intense isotropic absorption at $g \sim 2$ transition characteristic of tetrahedral FeCl_4^- .⁴⁴ The epr spectrum (Fig. V.11) provides an additional evidence for the suggested formulation $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]_2 \cdot \text{FeCl}_4$. A more detailed analysis of the epr spectra of all $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]_2\text{X}$ systems is in progress.

F. Conclusion

It is demonstrated that the Haao ligand can strongly bind iron(II) via azoimine chelation. The resulting $\text{Fe}(\text{aao})_3^-$ species appears to have a cis stereochemistry. The $\text{Fe}(\text{aao})_3^-$ unit acts as a versatile donor by virtue of the oximate oxygen atoms. It

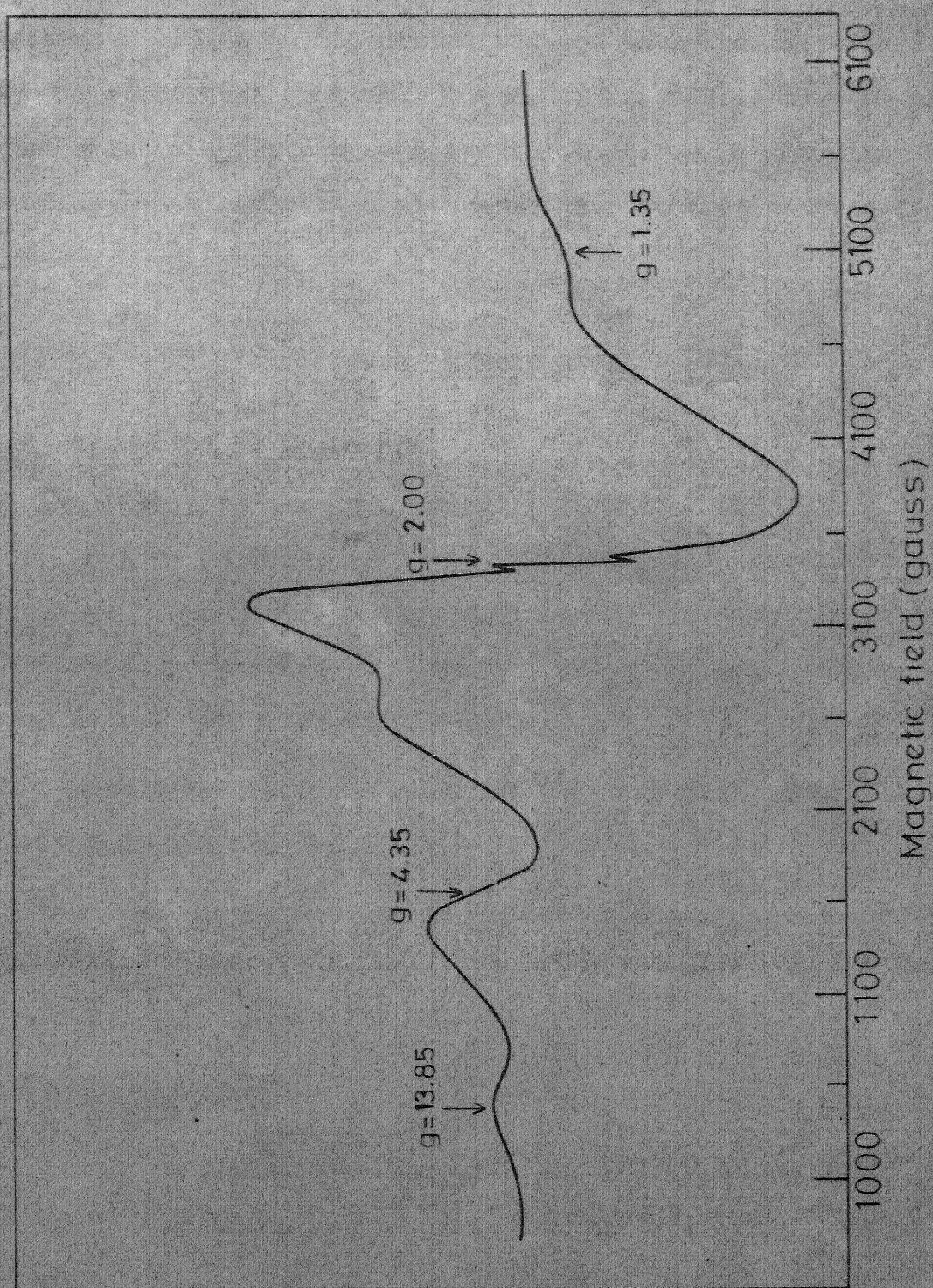


FIG. V.11 POWDER ELECTRON SPIN RESONANCE SPECTRUM OF $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$

($\text{R} = \text{p-CH}_3\text{-C}_6\text{H}_4$; $\text{Ar} = \text{C}_6\text{H}_5$)

binds H^+ , Na^+ , Ni^{2+} and Fe^{3+} (and a variety of other cations not discussed in this thesis). Mössbauer studies of the various systems would be quite interesting and would throw further light on the structural problem. Due to lack of facilities we have not been able to undertake such studies so far. We now plan these studies in collaboration with some laboratories elsewhere.

V.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Chemicals

Acetaldehyde was prepared by decomposing paraldehyde with a few drops of H_2SO_4 (concentrated) and carefully distilling it. Commercial n-butraldehyde, benzaldehyde, and p-tolualdehyde were used as such or after distillation.

n-Butylnitrite was prepared⁴⁵ by reacting n-butylalcohol with nitrous acid.

Commercial anhydrous iron(III) chloride was used in the reactions. Iron(II) perchlorate was prepared from iron powder and perchloric acid.

b. Ligands

Arylazooximes were prepared² by the nitrosation of aldehyde-arylhydrazone using butyl nitrite. The details are as follows:

i. Preparation of Aldehydephenylhydrazones

Phenylhydrazones of benzaldehyde and p-tolualdehyde were prepared by shaking aldehyde with phenylhydrazine (in 1:1 molar ratio) in acetic acid(20%). Pale yellow solid-formed was collected by filtration, washed with very dilute acetic acid, water-ethanol mixture and dried at 60°C).

Acetaldehydephenylhydrazone was prepared according to the procedure of Bamberger¹ with a little modification. The reaction was carried out at 0°C rather than at 10°C. In this way shining white crystals of hydrazone resulted with greater ease.

n-Butraldehydephenylhydrazone was prepared as follows:

0.2 mol of n-butraldehyde was cooled to subzero temperature in a freezing mixture. 0.2 mol of phenylhydrazine was added dropwise with continuous stirring and keeping the reaction mixture always below 0°C during the addition. The mixture was allowed to stand for another 15 min. 10 g of anhydrous sodium sulphate was then added. An orange oil separated which was collected and used as such.

ii. Arylazooximes from Aldehydephenylhydrazones

Arylazooximes with R= alkyl were prepared as follows:

0.03 mol of phenylhydrazone was dissolved in 30 ml ether. 0.2 mol of n-butylnitrite was added to the above solution which was then kept at room temperature. The reaction mixture which had turned dark reddish brown was extracted with 3x35 ml of 0.5 N aqueous

sodium hydroxide. The aqueous extract was cooled to 0°C and was then neutralised by dropwise addition of cold $1\text{ N H}_2\text{SO}_4$. During this process colour of the solution became progressively lighter and towards the end arylazooxime separated out as an orange crystalline solid. The orange solid was filtered, dried and the recrystallised from hexane. Yield was 25%.

Arylazooximes with $\text{R} = \text{aryl}$ were synthesised as described below: 0.1 mol of phenylhydrazone was dissolved in 150 ml of methanol (AnalaR grade). 0.2 mol of *n*-butylnitrite was added to it followed by 0.15 mol of potassium tertiary butoxide (or 0.2 mol of sodium methoxide). Immediately a red colouration developed. This mixture was heated to reflux for 1/2 hr and then cooled to room temperature and filtered. To the filtrate was added 0.15 mol of NaOH in 300 ml water. The mixture was kept for 4 hr in refrigerator and then extracted with ether. The aqueous layer was cooled to 0°C and neutralised with cold $1\text{ N H}_2\text{SO}_4$. The yellow crystalline solid formed was filtered, dried and recrystallised from hexane-dichloromethane mixture. Yield was 40%.

c. Preparation of $[\text{Fe}(\text{Fe}(\text{hao})_3)_2]\text{FeCl}_4$

Hao (0.015 mol) was dissolved in 30 ml ethanol (95%) and to it was added an ethanolic solution of anhydrous iron(III) chloride (0.01 mol in 20 ml). Immediately the colour darkened. The mixture was heated to boil. A crystalline solid started separating. The mixture was then cooled and filtered. The black

crystalline solid was washed thoroughly with benzene and then recrystallised from chloroform-ethanol mixture. The yield was 40%. However, we could not isolate a similar product when Haao with $R = CH_3$ was used.

d. Conversion of $[Fe(Fe(aao)_3)_2]FeCl_4$ to $NaFe(aao)_3 \cdot H_2O$

$[Fe(Fe(aao)_3)_2]FeCl_4$ (0.01 mol) was dissolved in 100 ml acetone and to it an aqueous solution of sodium hydroxide (0.03 mol in 15 ml water) was added dropwise. The mixture was warmed and stirred for 10-15 min. The mixture turned green and a brown precipitate of ferric hydroxide also deposited. The green solution was filtered, and the filtrate was concentrated. Shining green needle like crystals separated. These were collected by filtration and were recrystallised from acetone mixed with a very dilute aqueous sodium hydroxide.

e. Regeneration of $[Fe(Fe(aao)_3)_2]FeCl_4$ from $NaFe(aao)_3 \cdot H_2O$

$NaFe(aao)_3 \cdot H_2O$ (0.002 mol) was dissolved in 25 ml ethanol (95%) and to it was added an ethanolic solution of anhydrous iron(III) chloride (0.002 mol in 5 ml). The colour immediately turned greenish black. A black crystalline solid separated. This was found to be identical to $[Fe(Fe(aao)_3)_2]FeCl_4$.

f. Preparation of $HFe(aao)_3$ from $NaFe(aao)_3 \cdot H_2O$

$NaFe(aao)_3 \cdot H_2O$ (0.002 mol) was dissolved in 50 ml aqueous ethanol (50%). To this 0.0025 mol of HCl in 10 ml water was

added dropwise with stirring. Black precipitate of HFe(aao)_3 resulted. This was collected by filtration, washed several times with water and was then dried.

g. Conversion of HFe(aao)_3 to $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$

HFe(aao)_3 (0.002 mol) was dissolved in 15-20 ml acetone and an aqueous solution of sodium hydroxide (0.003 mol in 5 ml water) was added dropwise. The mixture turned green in colour. Gradual evaporation of acetone yielded shining green crystals of $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$.

h. Conversion of HFe(aao)_3 to $[\text{Fe}(\text{Fe(aao)}_3)_2]\text{FeCl}_4$

HFe(aao)_3 (0.002 mol) was taken in 50 ml ethanol and to it was added an ethanolic solution of anhydrous iron(III) chloride (0.002 mol, 5 ml). The mixture was heated to boil for 15 min. Shining black crystals of $[\text{Fe}(\text{Fe(aao)}_3)_2]\text{FeCl}_4$ were obtained.

i. Preparation of $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ for $\text{R} = \text{CH}_3$

Phenylazoacetaldoxime (0.03 mol) was dissolved in 50 ml ethanol (95%). An ethanolic solution of iron(III) chloride (0.02 mol) (or freshly prepared iron(III) acetate) was added to it. The reaction mixture was heated to boil. The black colour of the mixture deepened and a gummy mass separated. This was suspended in 40 ml of ethanol and treated with 0.03 mol of aqueous sodium hydroxide. An immediate green solution was obtained. The mixture

was warmed a little and filtered. The green solution was evaporated to dryness and was recrystallised from acetone-hexane or chloroform-hexane mixture. Shining green crystals were obtained in 50% yield.

j. Preparation of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$

HaaO (0.03 mol) was dissolved in 30 ml ethanol and to it was added an ethanolic solution iron(II) perchlorate (0.015 mol in 30 ml). Immediately the colour darkened. The mixture was heated to boil. A black crystalline solid settled on cooling. This was washed with benzene and then recrystallised from chloroform-ethanol mixtures. The yield was 40%.

k. Conversion of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ to $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$

$[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ (0.01 mol) was dissolved in 100 ml acetone and to it an aqueous solution of sodium hydroxide (0.03 mol in 15 ml water) was added dropwise. The mixture was warmed and stirred for 10-15 min. The mixture turned green and a brown precipitate of ferric hydroxide also deposited. The green solution was filtered and acetone was evaporated gradually. Shining green crystals of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ were obtained.

l. Regeneration of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ from $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$

$\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ (0.002 mol) was dissolved in 25 ml ethanol and to it was added an ethanolic solution of iron(III) perchlorate (0.001 mol in 5 ml). The colour immediately turned greenish

black. The mixture was heated to boil for 10 min. Black crystals of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ resulted.

B. Characterization of Complexes

This was done by C, H, N micro analyses and by metal analyses. Characterization data for all compounds are collected in Table V.12. Total iron was estimated gravimetrically as described in Chapter IV.

a. Amount of iron rejected from $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ and $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$ on addition of sodium hydroxide

150 mg of sample was dissolved in 50 ml acetone. 50 mg of NaOH was dissolved in 2 ml water and was added dropwise to the above solution. The mixture was stirred magnetically for 15 min and was then filtered through a sintered crucible. Four to five drops of sodium hydroxide solution was added to the filtrate and the mixture was filtered again to ensure the complete removal of ferric hydroxide rejected in the reaction. The ferric hydroxide was transferred to a beaker and was dissolved in 1 N HCl. 1.5 g of ammonium acetate in 70 ml water was added, followed by oxine reagent (2% in 1 N acetic acid) from a burette with constant stirring until a slight excess was present. About 6-7 ml was required. The dark precipitate thus obtained was digested on water-bath for 1 hr. It was filtered through a preweighed sintered crucible and washed successively with 1% acetic acid and water. It was dried

TABLE V.12

CHARACTERIZATION DATA^a

Compound	%C		%H		%N		%Fe	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
<u>NaFe(aao)₃·H₂O^b</u>								
1) R = CH ₃	49.40	50.18	4.46	5.10	21.61	21.70	9.57	8.72
2) R = \bar{n} -C ₃ H ₇	53.97	53.21	5.69	5.52	18.89	19.03	8.39	7.92
3) R = C ₆ H ₅	60.86	60.30	4.15	4.20	16.38	16.70	7.28	7.20
4) R = \bar{p} -CH ₃ -C ₆ H ₄	62.17	61.78	4.69	4.60	15.54	15.50	6.91	6.79
<u>HFe(aao)₃</u>								
5) R = \bar{n} -C ₃ H ₇	57.50	57.42	5.68	5.80	20.09	19.80	-	-
6) R = C ₆ H ₅	64.21	63.78	4.21	4.32	17.29	16.91	-	-
7) R = \bar{p} -CH ₃ -C ₆ H ₄	65.37	64.69	4.80	5.09	16.34	15.91	7.35	6.82
<u>[Fe(Fe(aao)₃)₂]FeCl₄^c</u>								
8) R = \bar{n} -C ₃ H ₇	47.80	47.53	4.78	4.85	16.73	16.90	14.80	14.49
9) R = C ₆ H ₅	54.73	54.46	3.51	3.71	14.73	14.55	13.01	13.05
10) R = \bar{p} -CH ₃ -C ₆ H ₅	56.18	57.04	4.01	4.36	14.04	13.79	12.46	12.56

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contd.,.

TABLE V.12 (CONTD.)

Compound	%C		%H		%N		%Fe	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
<u>$[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$</u>								
11) R = C_6H_5	58.09	57.91	3.75	3.85	15.64	15.44	10.53	10.59

a. In all the compounds Ar = C_6H_5

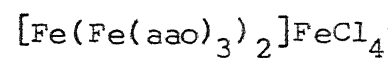
b. Percentage sodium in compounds (2) and (3), Calcd: 3.54 & 2.99;

Found: 3.71 & 2.81 respectively.

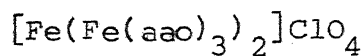
c. Percentage chloride in compounds (9) and (10), Calcd: 8.34 & 7.93;

Found: 8.12 & 7.59 respectively.

at 125-135°C to constant weight and weighed as $\text{Fe}(\text{C}_6\text{H}_5\text{OH})_3$.



Percentage of total iron present	= 13.05%
Weight of the compound taken for the iron rejection experiment	= 0.10702 g
Weight of the iron oxinate	= 0.06172 g
Percentage of iron rejected	= 6.69%
$\frac{\text{Total iron in the complex}}{\text{Rejected iron from complex}}$	= $\frac{13.05}{6.59} = 1.98$



Percentage of total iron present	= 10.53%
Weight of the compound taken for the iron rejection experiment	= 0.17265 g
Weight of the iron oxinate	= 0.05280 g
Percentage of iron rejected	= 3.49%
$\frac{\text{Total iron in the complex}}{\text{Rejected iron from the complex}}$	= $\frac{10.53}{3.49} = 3.01$

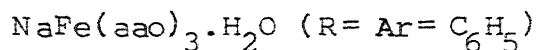
b. Estimation of Sodium⁴⁶

100 mg of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ was dissolved in 40 ml distilled water. 1N HCl was added till the green colour completely disappeared (the solid is $\text{HFe}(\text{aao})_3$; Na^+ remains in solution). The colourless solution was filtered and the residue was washed with water. The filtrate and the washings were collected in a China-dish and 8 ml of zincuranylacetate reagent was added. The

mixture was stirred magnetically for 1 hr and was then allowed to stand for 2 hr. A yellow crystalline precipitate thus obtained was filtered through a preweighed sintered crucible. The precipitate and the inside of crucible were washed thoroughly with washing solution and then once with ether. Air was drawn through the crucible to remove ether. The crucible was wiped with moist cloth and placed in the desiccator for 1 hr and weighed, as $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$. The weight was corrected as indicated by a blank determination carried through all steps of the above method.

Preparation of the reagent: 2 g of $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ and 5.56 g of zinc acetate was dissolved in 0.55 ml glacial acetic acid and 18 ml water. The solution was warmed until no further dissolution occurred, and was then cooled. A small precipitate of sodium salt precipitated out (impurity). The solution was allowed to stand for 24 hr and then filtered. Precaution was taken that the reagent was used at approximately the temperature prevailing at the time it was filtered.

Preparation of washing solution: Washing solution was prepared by adding 1 ml of acetic acid (30%) to 100 ml of ethanol (95%), shaking with a moderate excess of the triple salt, $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$ at room temperature and filtering.



Weight of the compound taken
for sodium analysis = 0.11245 g

Weight of $\text{NaZn(VO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$ = 0.21148 g

Percentage of sodium = 2.81%

Calculated percentage of
sodium = 2.99%

c. Chloride Estimation

80 mg of $[\text{Fe(Fe(aao)}_2)_2]\text{FeCl}_4$ was taken in a nickel crucible. 2 g of powdered potassium hydroxide and 1 g of potassium nitrate were added. The mixture was warmed slowly till it formed a melt. The melt was heated rigorously for another 20 minutes. The fused mass was extracted with water and filtered through a sintered funnel. The sintered funnel was washed with water several times. The filtrate and washings were collected together and acidified with dilute nitric acid. A solution of 0.1N AgNO_3 was then added dropwise till the precipitation was complete. The precipitate of AgCl was filtered through a preweighed sintered crucible and was washed 3-4 times with very dilute nitric acid and dried in hot air oven at 110°C .

C. Solvents

Details are given in Chapter II.

D. Physical Measurements

a. Electrical Conductance Measurements

Details are given in Chapter II.

b. Infrared Spectra

Details are given in Chapter II.

For the region $500\text{--}300\text{ cm}^{-1}$ spectra were recorded in nujol mull using polyethylene windows.

c. Electronic Spectra

Details are given in Chapter II.

d. Bulk Susceptibility Measurements

Details are given in Chapter II.

e. Electron Spin Resonance Spectra

Details are given in Chapter II.

f. Proton Magnetic Resonance Spectra

Pmr spectra were recorded at 100 MHz using a Varian HR-100 Spectrometer. Frequencies were measured by the usual side band technique. CDCl_3 was used as solvent and tetramethylsilane was used as an internal standard. Area measurements, where necessary were achieved Planimetrically.

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S U M M A R Y

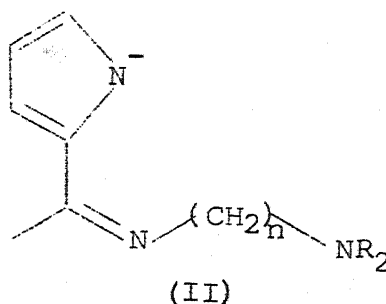
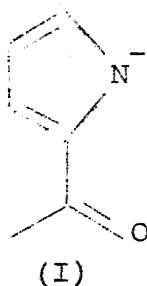
The chemistry described in this thesis can be broadly divided under two categories (i) mixed-ligand type and (ii) mixed-metal type. The materials presented in Chapters I-IV belong to the category (i), while those in Chapter V fall under category (ii).

I

A monomeric complex of formula $M(Lb)(Lt)$ (where Lb and Lt are potentially bidentate and tridentate ligands) in which all potentially coordinating atoms are bonded to metal will be pentacoordinated. In recent times this strategy has been used in our laboratory and elsewhere to design interesting systems. Not infrequently the $M(Lb)(Lt)$ system dimerises yielding pseudo-octahedral coordination. In other instances, adduct formation with donors bring about the same coordination geometry. In several cases the equilibrium between hexacoordinated and penta-coordinated geometry has been identified in solution. This area is reviewed in Chapter I.

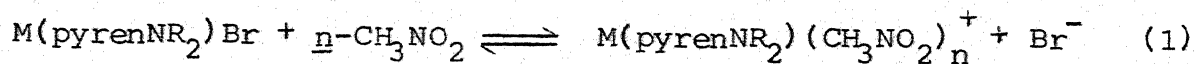
II

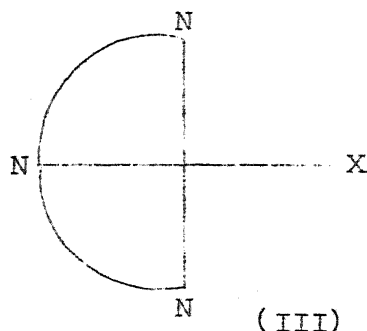
A new structural situation is described in Chapter II in which the ligand systems involved are pyrrole-2-aldehyde (Hpyr) and its Schiff base with $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NR}_2$ ($n = 2$ or 3). The conjugate base of these species are shown in I and II. I will abbreviated as pyr, while the abbreviation for II will be pyrenNR₂



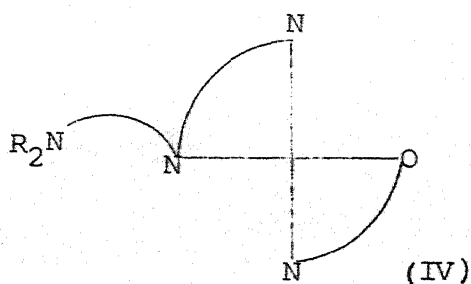
(when $n = 2$) and pyrtnNR₂ (when $n = 3$). The following systems have been obtained in the present work: $\text{M}(\text{pyrenNR}_2)\text{Br}$, $\text{M}(\text{pyrtnNR}_2)\text{Br}$, $\text{M}(\text{pyr})(\text{pyrenNR}_2)$, $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ ($\text{M} = \text{Cu}$ or Ni).

$\text{M}(\text{pyrenNR}_2)\text{Br}$ and $\text{M}(\text{pyrtnNR}_2)\text{Br}$: The nickel(II) system is diamagnetic while the copper(II) complexes have normal magnetic moment of ~ 1.8 BM. This and spectral results suggest the structure III. The most important point to note here is that both the ligand systems pyrenNR₂ and pyrtnNR₂ act in the tridentate fashion. The electrical conductivity data suggest that the compounds undergo partial dissociation in solution, probably due to reactions of the type



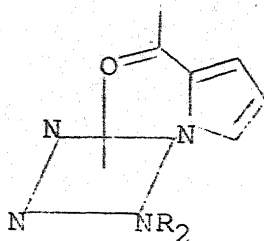


M(pyr)(pyrenNR₂): The infrared spectrum of Cu(pyr)₂ shows the C=O stretch at 1650 cm⁻¹, while Cu(pyrenNR₂)Br system described earlier, has the C=N stretch at ~ 1600 cm⁻¹. As expected the M(pyr)(pyrenNR₂) systems show both C=O and C=N stretches. Cu(pyr)-(pyrenNEt₂) was found to be monomolecular in freezing benzene. The mixed complexes could be either pentacoordinated belonging to the class M(Lb)(Lt) with all potential donor sites bound to the metal or tetraordinated and planar with bidentate pyrenNR₂ as in IV (NR₂ group is not coordinated to the metal). These complexes have normal magnetic moments. Ligand field spectra and ir data indicate that this system is actually tetraordinated.



More definitive evidence in favour of structure IV is obtained from studies of mixed crystal of Cu(pyr)(pyrenNMe₂) and Ni(pyr)(pyrenNMe₂). The most important observation is that the

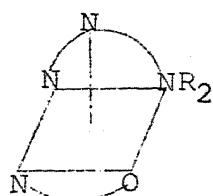
mixed crystals are isomorphous with pure $\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$, as determined from X-ray powder patterns and d-spacings. Since $\text{Ni}(\text{II})$ is diamagnetic and planar (IV) in the mixed crystal, it follows that the copper(II) species has also the geometry (IV) in the mixed crystal. Because of isomorphism, this is also true for the pure copper(II) complex. Thus $\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$ has the planar environment IV. Very dilute solution of $\text{Cu}(\text{pyr})(\text{pyrenNMe}_2)$ in $\text{Ni}(\text{pyr})(\text{pyrenNMe}_2)$ shows an axial epr spectrum with $g_{\parallel} = 2.199$; $g_{\perp} = 2.045$ and $A_{\parallel} = 187.0$ gauss; $A_{\perp} = 6.0$ gauss. Earlier we have categorised the various ways (dimerisation, adduct formation) by which pentacoordination may be hindered in a $\text{M}(\text{Lb})(\text{Lt})$ system. The pyrrole-2-alimine species described above, provide an example of a new situation where the potentially tridentate unit, actually acts only as bidentate ligand. We strongly suspect that the phenomenon is of steric origin. The ligand pyrenNR_2 in its tridentate mode will be able to span only in the meridional fashion due to the short length of the $-(\text{CH}_2)_2-$ chain. Models show that this brings the bidentate pyr moiety unfavourably close to the methyl groups of NMe_2 in pyrenNMe_2 in the hypothetical square pyramidal structure V. This steric hindrance leads to



(V)

the delinking of NMe_2 from the metal atom.

$\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$: If the above thesis regarding the steric effect in $\text{M}(\text{pyr})(\text{pyrenNR}_2)$ is correct, the complexes $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$ with a more flexible $-(\text{CH}_2)_3-$ chain may be penta-coordinated. In this potentially tridentate ligand can span facially. Models show that the configuration VI, is free from steric strain. With these ideas in mind the $\text{Cu}(\text{pyr})(\text{pyrtnNR}_2)$

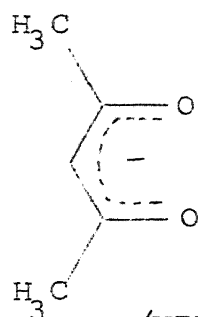


(VI)

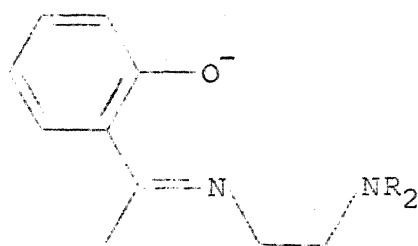
complexes were synthesised. They are monomolecular and have normal magnetic moments and ir spectra. Their d-d electronic spectra strongly suggest pentacoordinate geometry.

III

In our search for the pentacoordinated species of the type $\text{Ni}(\text{Lb})(\text{Lt})$, the reaction of bis(acetylacetonato)nickel(II), $\text{Ni}_3(\text{ac})_6$, with HsalenNR_2 was investigated earlier (ac and salenNR_2 are respectively the conjugate bases of acetylacetone (VII) and the Schiff base (VIII) of salicylaldehyde and $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NR}_2$). Square pyramidal species of the type $\text{Ni}(\text{ac})-(\text{salenNR}_2)$ were obtained. Having observed the dramatic stereochemical consequence of the $-(\text{CH}_2)_n-$ chain length in pyrrole-2-

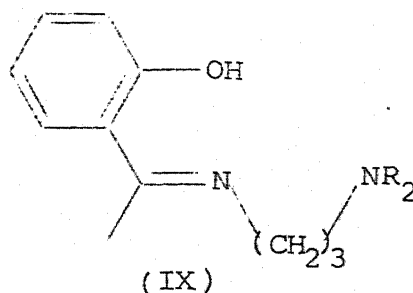


(VII)



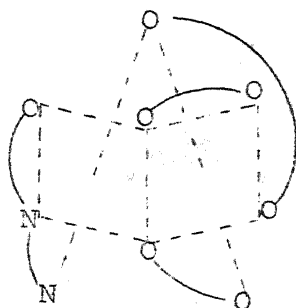
(VIII)

aldimine complexes, we undertook the investigation of the effect of this chain length on the composition and stereochemistry of some nickel(II) species. The systems, obtained by reacting $\text{Ni}_3(\text{ac})_6$ with HsaltnNR_2 (IX) are reported in Chapter III. These



(IX)

systems are of the type $\text{Ni}_2(\text{ac})_3(\text{saltnNR}_2)$. From magnetic susceptibility, ir and electronic spectral data it is concluded that each nickel(II) is in a pseudooctahedral environment. On the basis of model building it is proposed that $\text{Ni}_2(\text{ac})_3(\text{saltnNR}_2)$ has the structure X in which ac occupies bridging positions. It is known that the dinuclear fragment $\text{Ni}_2(\text{ac})_4$ is coordinatively unsaturated and yields adducts such as $\text{Ni}_2(\text{ac})_4(\text{pyridine})$ in which nickel(II) is octahedral. One may then expect that species of the type $\text{Ni}_2(\text{ac})_3(\text{tridentate})$ with octahedral nickel(II) should exist. The $\text{Ni}_2(\text{ac})_3(\text{saltnNR}_2)$ system provides an example. We have

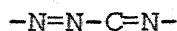


(X)

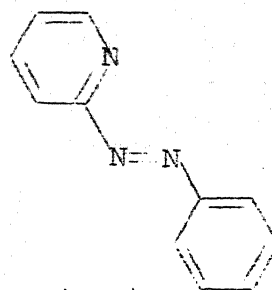
noted earlier that the reaction of $\text{Ni}_3(\text{ac})_6$ with salenNR_2 yields mononuclear pentacoordinate $\text{Ni}(\text{ac})(\text{salenNR}_2)$. No evidence for dinuclear species has been obtained with this ligand. The difference in the behaviour of salenNR_2 and saltnNR_2 can be rationalised on the basis of structure X. In this structure saltnNR_2 occupies three facial positions of an octahedron. The flexible $-(\text{CH}_2)_3-$ chain makes this possible. On the other hand salenNR_2 can only span in meridional positions due to relative shortness of the $-(\text{CH}_2)_2-$ chain. It cannot span facially.

IV

In Chapters IV and V the ligand systems used contain an azo group or more appropriately azoimine group XI. The results

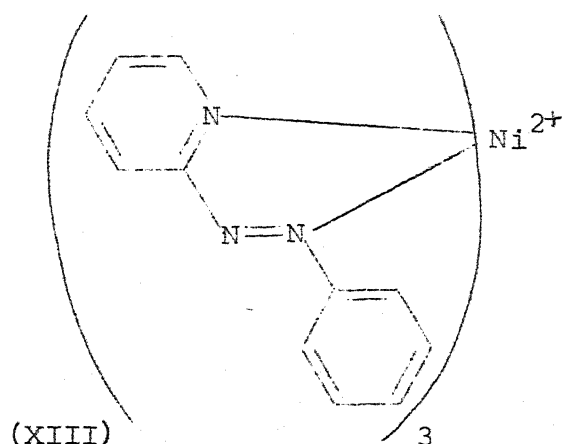


(XI)

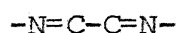


(XII)

obtained with 2-phenylazopyridine (pap) XII, form the subject matter of Chapter IV. The tris complexes $\text{Ni}(\text{pap})_3(\text{ClO}_4)_2$ and $\text{Fe}(\text{pap})_3\text{I}_2$ (these are not mixed-ligand complexes) behave as 1:2 electrolyte in solution. They contain the complex cation $\text{M}(\text{pap})_3^{2+}$. $\text{Ni}(\text{pap})_3^{2+}$ is fully paramagnetic and on the basis of electronic spectra has the octahedral structure XIII, with NiN_6



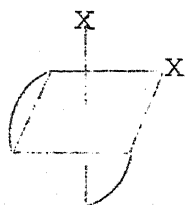
coordination sphere. $\text{Fe}(\text{pap})_3^{2+}$ is low-spin and is believed to have a similar structure. It shows an intense band in the visible region (~ 590 nm) which is assigned to the charge transfer transition $t_{2g} \rightarrow \pi^*$ (azoimine). The isoelectronic relationship between azoimine and diimine XIV, fragments are noted in this



(XIV)

context. The $t_{2g} \rightarrow \pi^*$ state also makes some contribution to the ground level also as is evident from ir data. The $\text{N}=\text{N}$ stretch is considerably lowered in $\text{Fe}(\text{pap})_3^{2+}$ in comparison to those in the free ligand and the nickel(II) complex.

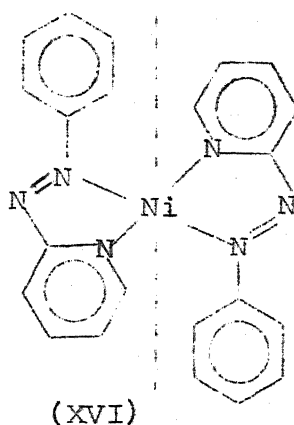
Nickel(II) forms mixed complexes of the type $\text{Ni}(\text{pap})_2\text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ ($\text{X} = \text{Cl}, \text{Br}$). These are fully paramagnetic in solid state and are only very slightly dissociated in solution. There is evidence that in systems of the type $\text{Ni}(\text{Lb})_2\text{X}_2$ (where Lb is a bidentate ligand), the cis configuration is preferred over the trans configuration, when X is widely separated from Lb in the spectrochemical series. In going from NiN_6 to trans- NiN_4X_2 , the octahedral ν_1 band shows an observable splitting due to decrease in symmetry from O_h to D_{4h} . The cis- NiN_4X_2 sphere has a lower symmetry (C_{2v}) than trans- NiN_4X_2 but the magnitude of orbital splitting is expected to be less. In practice such splitting is often not observed. The complexes of 2-phenylazo-pyridine under discussion shows an unsplit ν_1 band at 1090 nm. This taken in conjunction with other evidences has led us to propose the structure XV for $\text{Ni}(\text{pap})_2\text{X}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ species. The dichloromethane of crystallisation is strongly held in the



(XV)

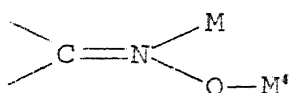
lattice and is not removed even at low pressure (5 mm) and elevated temperature (80°C). Quite a few transition metal complexes which contain dichloromethane of crystallisation are known. We wish to stress that the present compounds can also be prepared as amorphous powders without the dichloromethane of crystallisation.

On the other hand well formed crystals which are easy to purify are obtained when dichloromethane is present. The solid state infrared spectra of $\text{Ni}(\text{pap})_2\text{Br}_2$ and $\text{Ni}(\text{pap})_2\text{Br}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ were found to be essentially superimposable except that the latter compound shows bands characteristic of dichloromethane also. The dichloromethane of crystallisation does not appear to affect the ligand disposition in any major way. Now we turn to $\text{Ni}(\text{pap})_2\text{I}_2$ which is diamagnetic and shows no ligand field bands below 700 nm. In this complex the $\text{Ni}(\text{pap})_2$ sphere is grossly planar presumably with a trans (steric overcrowding of phenyl groups in cis geometry) disposition of ligand molecules XVI. The iodide ions

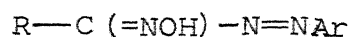


remain partially bound (weak axial coordination) in solution, since the observed electrical conductivity is much lower than that expected for a 1:2 electrolyte. In view of the proposed difference in stereochemistry of $\text{Ni}(\text{pap})_2$ fragment in the chloro (or bromo) and iodo complexes, it may be significant that the -N=N- stretch in former (no centre of symmetry) is more intense than that of the latter (centre of symmetry).

In the last chapter (Chapter V) mixed-metal complexes of the type XVII, (where M and M' could be two different metal ions or it could be the same metal ion in two different oxidation states) derived from arylazooximes (Hao) XVIII, are described. This class of

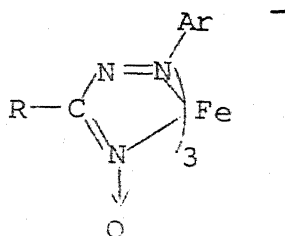


(XVII)



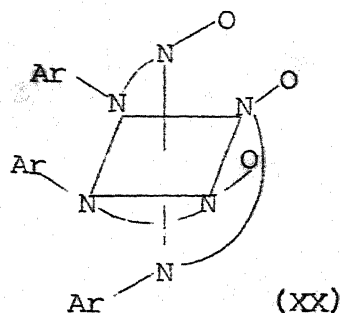
(XVIII)

ligand has a strong affinity for iron(II). The low-spin (t_{2g}^6) anionic tris chelate $Fe(aao)_3^-$ contains five membered chelate rings (ir data), XIX and is green in colour due to the presence



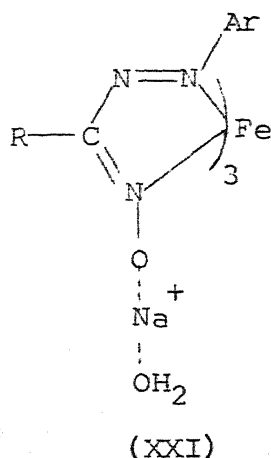
(XIX)

of a strong $t_{2g} \rightarrow \pi^*$ (azoimine) charge-transfer transition at ~ 600 nm. This ion can be isolated in the form of a sodium salt $NaFe(aao)_3 \cdot H_2O$ in which $Fe(aao)_3^-$ has (pmr data) cis geometry XX.



(XX)

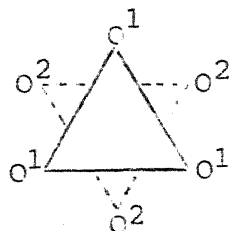
The sodium ion is believed to be bound to water molecule and to oximate oxygen atoms as shown schematically in structure XXI. $\text{NaFe(aao)}_3 \cdot \text{H}_2\text{O}$ is poorly conducting in nitromethane solution. It is soluble in a variety of organic solvents including benzene.



On reaction with acid it produces HFe(aao)_3 in which the proton is believed to be chelated (intermolecularly or intramolecularly) to Fe(aao)_3^- via the oxime oxygen atoms.

Our researches in iron complexes of arylazooximes originated from the attempted reaction of HaaO with anhydrous FeCl_3 in ethanol. An unusual reaction occurs in which part of Fe^{3+} is reduced to Fe^{2+} and a crystalline solid deposits. This has been shown to be an intervalence species of the type $[\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}}(\text{aao})_3)_2]^-$ $\text{Fe}^{\text{III}}\text{Cl}_4$ (1:1 electrolyte in nitromethane and nitrobenzene solutions). In this both iron(III) atoms are high-spin (five unpaired electrons) while iron(II) is low-spin. The iron(III) atom in the cation is believed to be bound in an octahedral fashion to the six oximate oxygen atoms of two cis- Fe(aao)_3^- moieties. This is shown

schematically in XXII in which the oxygen atoms coming from the same $\text{Fe}(\text{aao})_3$ unit carry the same number on the top. The Fe-O



(XXII)

for the FeO_6 coordination sphere is observed at $\sim 430 \text{ cm}^{-1}$. The ν_3 band of FeCl_4^- anion is present at $\sim 380 \text{ cm}^{-1}$. The corresponding perchlorate $[\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}}(\text{aao})_3)_2]\text{ClO}_4$ results from a direct reaction between iron(II) perchlorate and H_{aao}. In the infrared Fe-O stretch is again seen at $\sim 430 \text{ cm}^{-1}$ (the presence of a shoulder at $\sim 400 \text{ cm}^{-1}$ suggests distortion from an octahedral geometry). Infrared data supports the presence of a completely ionic tetrahedral ClO_4^- . The species $[\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}}(\text{aao})_3)_2]\text{Br}$ is also briefly reported. The $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ ($\text{X} = \text{ClO}_4, \text{Br}$) shows a $g' \sim 4.3$ epr line characteristic of rhombic FeO_6 sphere. When $\text{X} = \text{FeCl}_4$, an intense additional band at $g \sim 2.0$ (due to FeCl_4^-) is also observed.

The chemical interconversion of the various species viz., $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$, $\text{HFe}(\text{aao})_3$, $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ and $\text{Fe}(\text{Fe}(\text{aao})_3)_2 - \text{ClO}_4$ are described. For example $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$ reacts with sodium hydroxide to yield two moles of $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ and two moles of iron(III) hydroxide. On the other hand $\text{NaFe}(\text{aao})_3 \cdot \text{H}_2\text{O}$ reacts with one mole of FeCl_3 to regenerate $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$. Since

$[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{X}$ ($\text{X} = \text{FeCl}_4$ or ClO_4) contain both iron(II) and iron(III) linked by a bridge system one may expect a low-energy intervalence charge transfer transition: $\text{Fe}(\text{II}) \rightarrow \text{Fe}(\text{III})$ (class II mixed valence system). However in practice we have not been able to locate such an intervalence bond. It is believed that this band lies under the very intense ~ 600 nm iron(II) \rightarrow ligand transition making a direct observation impossible.

A species of the type $\text{Ni}[\text{Fe}(\text{aao})_3]_2$ is briefly reported. This is believed to have a structure similar to that of $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]^+$ with Fe^{3+} replaced by Ni^{2+} . The $\text{Fe}(\text{aao})_3^-$ thus acts as versatile donor by virtue of oximate oxygens. It binds H^+ , Na^+ , Ni^{2+} and Fe^{3+} and a variety of other metal ions which are not considered in this thesis.

VITAE

Born on January 14, 1949 at Chickmagalur (Karnataka), the author obtained his B.Sc. (Hons.) and M.Sc. degrees from Bangalore University in 1969 and 1971 respectively. He joined the Ph.D. programme of the Department of Chemistry, Indian Institute of Technology, Kanpur in 1972. He is presently continuing in the same Institute as a Research Assistant.